

## REVIEWS

# Real-Gas Properties of $n$ -Alkanes, $O_2$ , $N_2$ , $H_2O$ , $CO$ , $CO_2$ , and $H_2$ for Diesel Engine Operation Conditions\*

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**Abstract**—The objective of the research outlined in this paper was to develop the analytical approximations for calculating real-gas properties ( $p$ – $v$ – $T$  data, thermodynamic functions: internal energy, enthalpy, and entropy, and specific heats) of vapor-phase  $n$ -alkanes from  $C_1$  (methane) to  $C_{14}$  (normal tetradecane),  $O_2$ ,  $N_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$ , and  $H_2$  within the range of pressure  $0.05 \text{ MPa} \leq p \leq 20 \text{ MPa}$  and temperature  $280 \text{ K} \leq T \leq 3000 \text{ K}$  aimed for implementation into computational fluid dynamics (CFD)-codes simulating the operation process in modern Diesel engines. The analytical approximations have been developed based on available literature data and on the new equation of state for moderately dense gases. The approximations reported are rather simple and therefore can be used directly in CFD codes. Approximations for mixing rules are also provided.

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## NOMENCLATURE

$A_1, A_2, \dots$ —coefficients for individual species
$b = \lambda RT_c/p_c$
$\bar{b} = bp_c = \lambda/Z_c$
$B$ —second virial coefficient
$B_g = B/\mu$ —second virial coefficient
$\bar{B} = B\rho_c$ —dimensionless second virial coefficient
$\bar{B}_1 = \tau \frac{d\bar{B}}{d\tau}$ —dimensionless first logarithmic derivative of second virial coefficient
$\bar{B}_2 = \tau \frac{d\bar{B}_1}{d\tau}$ —dimensionless second logarithmic derivative of second virial coefficient
$\bar{B}_s \equiv d(\tau \bar{B})/d\tau = \bar{B} + \bar{B}_1$
$\bar{B}_{2t} \equiv d(\tau \bar{B}_1)/d\tau = \bar{B}_1 + \bar{B}_2$
$C$ —coefficient in thermal equation of state
$C_g = C/\mu$ —coefficient in thermal equation of state
$\bar{C} = C\rho_c^2$ —dimensionless coefficient in thermal equation of state
$C_{p0}$ —ideal-gas specific heat at constant pressure
$C_{v0}$ —ideal-gas specific heat at constant volume
$C_{p, exc}$ —excess specific heat at constant pressure
$C_{v, exc}$ —excess specific heat at constant volume
$C_p$ —real-gas specific heat at constant pressure
$C_v$ —real-gas specific heat at constant volume
$D$ —coefficient in thermal equation of state
$D_g = D/\mu$ —coefficient in thermal equation of state

$\bar{D} = D\rho_c^3$ —dimensionless coefficient in thermal equation of state

$E$ —real-gas internal energy

$E_0$ —ideal-gas internal energy

$E_{exc}$ —excess internal energy

$F$ —coefficient in thermal equation of state

$\bar{F} = F\rho_c^4$ —dimensionless coefficient in thermal equation of state

$G$ —coefficient in thermal equation of state

$\bar{G} = G\rho_c^5$ —dimensionless coefficient in thermal equation of state

$H$ —real-gas enthalpy

$H_0$ —ideal-gas enthalpy

$H_{exc}$ —excess enthalpy

$I$ —coefficient in thermal equation of state

$\bar{I} = I\rho_c^6$ —dimensionless coefficient in thermal equation of state

$p$ —pressure

$p_c$ —critical pressure

$r = \rho/\rho_c$ —dimensionless density

$R$ —universal gas constant

$R_g = R/\mu$ —universal gas constant

$S$ —real-gas entropy

$S_0$ —ideal-gas entropy

$S_{exc}$ —excess entropy

$T$ —temperature

$T_0$ —reference temperature

$T_c$ —critical temperature

$x = \theta/T$ —dimensionless reciprocal temperature

$x_i = \theta_i/T$  ( $i = 1, 2, 3, 4$ )—dimensionless reciprocal temperature

$x_0 = \theta/T_0$ —dimensionless reciprocal reference temperature

$x_{i0} = \theta_i/T_0$  ( $i = 1, 2, 3, 4$ )—dimensionless reciprocal reference temperature

$Z_c = p_c/(\rho_c RT_c)$ —compressibility in the critical point

### Greek Symbols

$\lambda$ —fitting parameter

$\mu$ —molecular mass

$\Pi = p/p_c$ —dimensionless pressure

$\rho$ —density

$\rho_c$ —critical density

$\tau = T/T_c$ —dimensionless temperature

$\theta, \theta_1, \theta_2, \theta_3, \theta_4$ —characteristic vibration temperatures of molecule

combustion, pollutant formation) CFD methods are becoming more and more important. Predictability can only be reached with detailed physical and chemical submodels. The basis for state-of-the-art CFD codes is still the assumption of ideal gas properties. In the codes, transient conservation equations (for species, momentum, energy, turbulence, etc.) are closed by the use of the ideal-gas equation of state (EOS)

$$\frac{pV}{RT} = 1,$$

where  $p$  is pressure,  $V$  is the molar volume,  $R$  is the gas constant, and  $T$  is the temperature.

Within the ideal gas approximation, the specific molar internal energy,  $E_0$ , and enthalpy,  $H_0$ , are the functions of temperature:

$$\begin{aligned} E_0 &= E_0(T), \\ H_0 &= H_0(T), \end{aligned} \quad (1)$$

or, in the differential form,

$$\begin{aligned} dE_0 &= C_{v0}(T)dT, \\ dH_0 &= C_{p0}(T)dT, \end{aligned}$$

where  $C_{v0}$  and  $C_{p0}$  are the ideal-gas specific heats at constant volume and at constant pressure, respectively.

The assumption of ideal gas behaviour is known to be valid for low-density gases, when interaction of molecules is negligible. However, thermodynamic conditions in modern combustion engines may be out of the range of validity of the ideal gas approximation, in particular in local regions with high pressure and low temperature (e.g., in Direct Injection Diesel engine the peak pressure attains the value of 18 MPa, while the temperature in the cylinder at this pressure can vary locally from about 1200 to 2800 K depending on whether unburned pockets of fuel-air mixture or combustion products are considered; moreover, in the near-wall regions, the temperature may be as low as 400–500 K due to cooling at cylinder walls). Clearly, at these conditions, real gas effects must be taken into account. The enthalpies and other thermodynamic functions of real gases are available as the tables of thermophysical properties and correlations (see, e.g., [1–11]).

The data attributed to different substances under discussion are allocated in corresponding chapters. Since for some of them the analysis presented here can be meaningful by itself (irrespective to the CFD calculations related to the processes in engines), each chapter is written in a complete and integrate form that allows one to consider it separately.

In thermodynamic and technical calculations various systems and units of measure related to the values and parameters considered here are used. In order to exclude a systematic error concerned with conversion of experimental values from one system into another, experimental data and suggested calculation schemes are presented in the units, which are initially used in

## INTRODUCTION

For the development of combustion strategies in internal combustion engines and for simulating in-cylinder processes (gas exchange, mixture formation,

original publications and/or which can be used in practice. Nevertheless, in all cases where it is possible without additional systematic errors, the SI units are used.

In the literature, the real-gas EOS is often formulated in terms of the virial EOS:

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \frac{E}{V^4} + \frac{F}{V^5} + \dots, \quad (2)$$

where  $B, C, D, E, F, \dots$  are the virial coefficients that are the functions of temperature. The virial coefficients  $B, C, D, E, F, \dots$  are referred to as second, third, fourth, etc. virial coefficients. The first virial coefficient is nondimensional and is equal to unity. The virial coefficients in Eq. (2) have different dimensions. For the ideal gas, all terms with virial coefficients, beginning from the second, are negligibly small.

The applicability of Eq. (2) is evidently determined by convergence of the power series of  $(1/V)$ . For liquids, as well as for the matter at the critical point, the virial expansion of Eq. (2) is known to diverge. The virial EOS is most useful for gases of low and moderate density, when  $(1/V)$  can be considered as a small parameter and the expansion terms rapidly decrease.

To apply the virial EOS, the dependencies of the virial coefficients on temperature have usually to be obtained experimentally. These dependencies are different for different species. At a given temperature, the virial coefficients can be obtained by fitting Eq. (2) to the experimental data on the isothermal  $p$ – $V$ -dependencies.

There exist a number of approximations for the real-gas EOS that differ from the virial EOS (2). One of the most popular equations of this type used in modern CFD codes is the Redlich–Kwong equation (or its numerous modifications):

$$p = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}, \quad (3)$$

where  $a$  and  $b$  are the parameters for the individual species depending on the values of critical pressure and temperature. In case the parameters  $a$  and  $b$  are available, the pressure curve given by Eq. (3) can be approximated with Eq. (2) and the least required virial coefficients can be obtained.

Internal energy and other thermodynamic functions of a real gas differ from those relevant to the ideal gas. For determining real-gas properties, a concept of excess thermodynamic functions, e.g., excess internal energy  $E_{exc}(T, \rho)$ , is used:

$$E_{exc}(T, \rho) = - \int_0^\rho [T(\partial p / \partial T)_\rho - p] d\rho / \rho^2, \quad (4)$$

where  $\rho$  is the molar density ( $\rho = 1/V$ ). Based on Eqs. (1), (2), and (4) one can determine the real-gas internal energy in the form of the sum of the ideal-gas energy  $E_0(T)$  and the excess energy  $E_{exc}(T, \rho)$ :

$$E(T, \rho) = E_0(T) + E_{exc}(T, \rho). \quad (5)$$

Using available experimental and computational data, it appears possible to determine (with certain accuracy) the real-gas properties of individual gaseous species relevant to operating conditions of Diesel engine. Under conditions relevant to modern Diesel engines, other than real-gas effects can also play a significant role. Among them are (i) two-phase equilibrium effects, (ii) effects of gas-phase chemical decomposition of fuel molecules, and (iii) effects of dissociation and ionization. As the derivation of real-gas EOS is expected to be considerably complicated with taking into account two-phase equilibrium effects and the effects of dissociation and ionization (there are no available approaches in the literature, and a particular analytical study should be undertaken), these effects have to be neglected at the first stage of the study.

The objective of the research outlined in this paper is to develop analytical approximations for calculating real-gas properties (specific volume, internal energy or enthalpy) of individual gaseous species  $O_2, N_2, H_2O, CO_2, H_2$ , and  $CO$ , and vapour-phase  $n$ -alkanes from  $C_1$  (methane) to  $C_{14}$  (normal tetradecane) within the range of pressure  $0.05 \text{ MPa} \leq p \leq 20 \text{ MPa}$  and temperature  $280 \text{ K} \leq T \leq 3000 \text{ K}$  aimed for implementation into the CFD-codes simulating the operation process of internal combustion engines.

To meet the above objective, the virial EOS for gaseous  $n$ -alkanes and other compounds like  $O_2, N_2, CO, CO_2, H_2O$ , etc. should be provided which would be applicable for pressures up to 20 MPa and temperatures up to 3000 K. Regarding the upper temperature level, a reasonable upper level for  $n$ -alkanes is less than 1000–1500 K, in particular for heavy  $n$ -alkanes, due to thermal instability of these hydrocarbons at elevated temperatures. Other compounds of interest ( $O_2, N_2, CO, CO_2, H_2O$ , etc.) can be considered as relatively stable even at a temperature of 3000 K. Formally, the validity of EOS and temperature dependencies of thermodynamic functions will not be limited by the prescribed upper temperature limit (3000 K), however the accuracy of corresponding approximations at higher temperatures can deteriorate. The temperature range within which the accuracy of the approximations is most favorable depends on gas density. This range is widest for rarefied gases whose properties are close to the ideal gas properties.

High pressures of order of 10 MPa are attained in engine cylinders in the course of simultaneous compression and heating. The gas, which is initially at normal ambient conditions and has a density of about  $3 \times 10^{19}$  particles/cm<sup>3</sup>, is compressed no more than by a factor of 100. In this case, the density of compressed gas does not exceed a fraction of 0.1 of liquid density and 0.3 of the critical density. Therefore, in view of engine applications and keeping in mind the objectives of obtaining the virial EOS in the form of a truncated power series of density, we will seek for the

EOS meeting the requirement on accuracy ( $\Delta p/p \leq 1\%$  at given values of temperature and density) only at densities  $\rho \leq 0.4\rho_c$ , where  $\rho_c$  is the critical density. The parametric domain at the  $p$ – $v$  plane, where the EOS has to meet these preset requirements on the accuracy ( $\Delta p/p \leq 1\%$ ) is shown in Fig. 1 on the example of propane.

## CHAPTER 1: NORMAL ALKANES

### 1.1. Equation of State for *n*-Alkanes

Depending on the accuracy required for determining the  $p$ – $\rho$ – $T$  properties of real gases, including gaseous *n*-alkanes, different model equations are usually used. If the task is to determine pressure with the accuracy of the order of 10% at given values of molar volume,  $v$ , and temperature,  $T$ , or to determine the molar volume,  $v$ , (or the molar density  $\rho$ ) with the same accuracy at given values of pressure,  $p$ , and temperature,  $T$ , the so called “co-volume” EOS of the Van der Waals type are usually applied. These equations, e.g., Van der Waals equation itself, Redlich–Kwong equation (see Eq. (3)), Peng–Robinson equation, etc., include two to three parameters. These parameters are determined based on experimental  $p$ – $v$ – $T$  data. Such data that are validated by different researchers and well documented, are usually available for temperatures up to 1000–1500 K (for substances that are thermally stable at these temperatures) and pressures up to several hundreds of MPa with the accuracy of the order of 1%.

To approximate the  $p$ – $\rho$ – $T$  data theoretically with the accuracy of experimental data, multiparameter EOS are used. In handbooks and textbooks considering lower hydrocarbons of alkane homology (from methane to *n*-hexane), the  $p$ – $\rho$ – $T$  EOS containing few tens (40–50) of parameters are reported. As a matter of fact, such multiparameter equations are nothing else as complex mathematical interpolations of experimental data. The use of such equations in CFD is associated with growing computational costs, as the EOS should be used in each control volume, at each iteration of each time step. Moreover, such equations have been reported only for lower *n*-alkanes. Hence such multiparameter EOS appear to be hardly appropriate for CFD purposes.

However, if one does not seek very accurate representation of experimental data in the close vicinity to the critical point (in terms of temperature this vicinity is  $\pm(2-3)$  K), the number of fitting parameters in the multiparameter EOS can be considerably decreased while the accuracy of  $p$ – $\rho$ – $T$  data approximations will remain comparable with the accuracy of experimental data. For this purpose, several EOS containing about 10 parameters have been suggested. When applied to hydrocarbons and to a number of other real gases, the Benedict–Webb–Rubin (MBWR) equation [6] modified by Starling and Kwok (SK) [12] appeared to be the

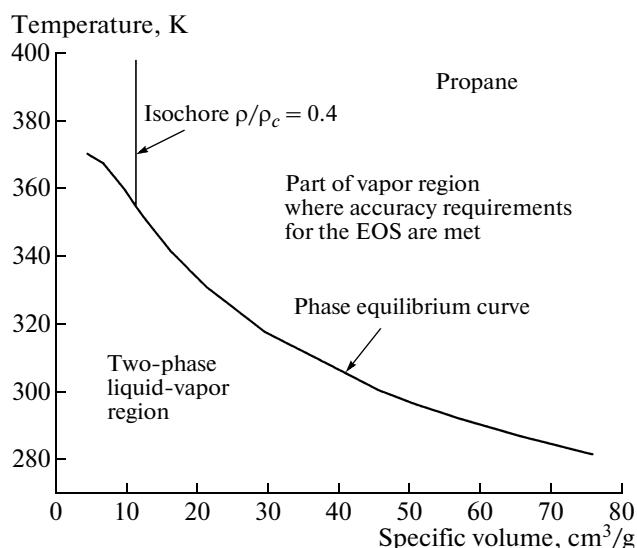


Fig. 1. Parametric domain at the  $p$ – $v$  plane, where the EOS has to meet the preset requirements on the accuracy ( $\Delta p/p \leq 1\%$ ).

most suitable equations of this type. The SK equation contains 11 parameters and is given in the form:

$$p = \rho RT + \left( B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho^2 + \left( RTb - a - \frac{d}{T} \right) \rho^3 + \alpha \left( a + \frac{d}{T} \right) \rho^6 + \frac{c\rho^3}{T} (1 + \gamma\rho^2) \exp(-\gamma\rho^2). \quad (6)$$

The parameters entering Eq. (6) for eight *n*-alkanes—from methane to *n*-octane—are presented in the series of papers by Starling and Kwok [13–16] and reproduced here in Table 1. The units for these parameters correspond to pressure in psia, temperature in °R, and molar density in lb.-mol/cu.ft. The gas constant in these units is equal to  $R = 10.7335$ . If density and temperature are taken in mol/dm³ and Kelvin, then substitution of density and temperature in Eq. (6) should be accompanied with multiplication of their values by 0.06248 and 1.8, respectively. To translate the resultant pressure to units of MPa, one has to divide the result given by Eq. (6) by 145.03774.

The MBWR equation was further modified by Younglove and Ely [17]. Their modified EOS contains 31 parameters. The values of these parameters were obtained for first four alkanes, from methane to *n*-butane. This modification provides a considerably more accurate approximation for experimental data in the liquid phase and makes the EOS applicable in wider ranges of thermodynamic parameters. Based on this EOS, various thermodynamic functions were calculated and tabulated in [17] for four alkanes mentioned above.

**Table 1.** Parameters entering Eq. (6) for different *n*-alkanes

	Methane	Ethane	Propane	<i>n</i> -Butane	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane
$A_0$	7520.29	13439.3	18634.7	32544.7	51108.2	45333.1	77826.9	81690.6
$B_0$	0.723251	0.826059	0.964762	1.56588	2.44417	2.66233	3.60493	4.86965
$C_0$	$271092 \times 10^3$	$295195 \times 10^4$	$796178 \times 10^4$	$137436 \times 10^5$	$223931 \times 10^5$	$526067 \times 10^5$	$615662 \times 10^5$	$996546 \times 10^5$
$D_0$	$107737 \times 10^5$	$257477 \times 10^6$	$453708 \times 10^6$	$333159 \times 10^6$	$101769 \times 10^7$	$552158 \times 10^7$	$777123 \times 10^7$	$790575 \times 10^7$
$E_0$	$301122 \times 10^5$	$146819 \times 10^8$	$256053 \times 10^8$	$230902 \times 10^7$	$390860 \times 10^8$	$626433 \times 10^9$	$636251 \times 10^7$	$346419 \times 10^8$
$A$	2574.89	22404.5	40066.4	71181.8	162185	434517	359087	131646
$\alpha$	0.468828	0.909681	2.01402	4.00985	7.06702	9.70230	21.8782	34.5124
$B$	0.925404	3.11206	5.46248	9.14066	16.6070	29.4983	27.4415	10.5907
$C$	$437222 \times 10^3$	$681826 \times 10^4$	$274461 \times 10^5$	$700044 \times 10^5$	$135286 \times 10^6$	$318412 \times 10^6$	$374876 \times 10^6$	$642053 \times 10^6$
$D$	47489.1	702189	$150520 \times 10^2$	$364238 \times 10^2$	$388521 \times 10^2$	$327460 \times 10^2$	8351150	$185906 \times 10^3$
$\gamma$	1.48640	2.99656	4.56182	7.54122	11.8593	14.8720	24.7604	21.9888

The equations of the type of Eq. (6) can be readily used for CFD purposes. Nevertheless, such equations seem to be too complex for the applications dealing with automotive engines exhibiting relatively low compression densities. Again, such equations are available only for lower hydrocarbons. For higher hydrocarbons, the parameters of the EOS remain unknown and the recommendations on their derivation (see, e.g., [18]) are somewhat ambiguous and seem insufficiently reliable.

In view of the apparent complexity and incompleteness of available EOS for *n*-alkanes (up to *n*-tetradecane), we have developed another EOS, which is unique for all *n*-alkanes and is comparatively simple (i.e., contains less parameters than Eq. (6)). Our EOS has the form of the virial series with a limited number of terms and is suitable for CFD applications. In this EOS, individual properties of different *n*-alkanes are represented only by their critical parameters ( $p_c$ ,  $T_c$ , and  $\rho_c$ ) and Pitzer factors. Additional four parameters of the EOS are common for all *n*-alkanes.

Short description of its derivation procedure is given below in Section 1.2. We also provide the other equivalent form of the new EOS. The accuracy of predicting pressure,  $p$ , at given values of temperature,  $T$ , and density,  $\rho$ , is illustrated by comparing with available experimental data.

### 1.2. Equation of State Derivation Procedure and Accuracy Tests

At relatively low densities, the accuracy of the Van der Waals EOS can be considerably improved by replacing the original expression for the second virial coefficient,  $B$ , with a more precise expression obtained by Ruzicka and Majer [19] for *n*-alkanes:

$$B = RT_c/p_c[f_0 + \omega f_1], \quad (7)$$

where

$$f_0 = 0.14445 - 0.33/\tau - 0.1385/\tau^2 - 0.0121/\tau^3 - 0.000607/\tau^8, \quad (8)$$

$$f_1 = 0.0637 + 0.331/\tau^2 - 0.423/\tau^3 - 0.008/\tau^8, \quad (9)$$

$\tau \equiv T/T_c$  is the reduced temperature, and  $\omega$  is the Pitzer factor (see Table 2). The virial EOS with four virial coefficients left is taken in the form:

$$p = \rho RT[1 + B(T)\rho + b^2\rho^2 + b^3\rho^3], \quad (10)$$

where  $\rho$  is the molar density (number of moles in a unit volume) related to molar volume,  $v$ , as  $\rho = 1/v$ , and  $b$  is the co-volume entering term  $RT/(v - b)$  in the Van der Waals EOS. This latter parameter can be represented as a combination of critical parameters taken in proper dimension (e.g., dimension of molar volume):

$$b = \lambda RT_c/p_c, \quad (11)$$

where  $T_c$  and  $p_c$  are the critical temperature and pressure, and  $\lambda$  is the numerical coefficient (for example, in Peng–Robinson equation,  $\lambda = 0.078$ ). In terms of dimensionless pressure, temperature, and density defined as

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c,$$

where  $\rho_c$  is the critical molar density, Eq. (10) can be transformed to

$$\Pi = Z_c^{-1} r \tau [1 + \bar{B}r + (\bar{b}r)^2 + (\bar{b}r)^3]. \quad (12)$$

Here,

$$\bar{B} \equiv R p_c, \quad (13)$$

$$\bar{b} \equiv b \rho_c \equiv \lambda/Z_c, \quad (14)$$

and  $Z_c \equiv p_c/(\rho_c RT_c)$  is the critical compressibility.

Further improvement of accuracy of Eq. (10) in the parametric domain where two first terms in square brackets are not sufficient may be attained for each *n*-alkane by introducing the dependence of coefficient  $\lambda$  on temperature and density. Making such a correction for one of *n*-alkanes (referred conditionally to as

**Table 2.** Critical parameters and Pitzer factors

<i>n</i> -Alkane	$T_c$ , K	$p_c$ , MPa	$\rho_c$ , mol/dm <sup>3</sup>	$\omega$
Methane	190.53 [17]	4.59797 [17]	10.150 [17]	0
Ethane	305.34 [17]	4.87143 [17]	6.875 [17]	0.098 [6]
Propane	369.85 [17]	4.24766 [17]	5.000 [17]	0.152 [6]
<i>n</i> -Butane	425.16 [17]	3.796 [17]	3.920 [17]	0.193 [6]
<i>n</i> -Pentane	469.7 [19]	3.370 [19]	3.216 [2]*	0.251 [19]
<i>n</i> -Hexane	507.6 [19]	3.025 [19]	2.711 [2]*	0.299 [19]
<i>n</i> -Heptane	540.2 [19]	2.74 [19]	2.336 [2]*	0.350 [19]
<i>n</i> -Octane	568.7 [19]	2.49 [19]	2.200 [2]*	0.397 [19]
<i>n</i> -Nonane	594.6 [19]	2.29 [19]	1.840 [2]*	0.443 [19]
<i>n</i> -Decane	617.7 [19]	2.11 [19]	1.659 [2]*	0.490 [19]
<i>n</i> -Undecane	639 [19]	1.98 [19]	1.516 [2]*	0.533 [19]
<i>n</i> -Dodecane	658 [19]	1.82 [19]	1.391 [2]*	0.573 [19]
<i>n</i> -Tridecane	675 [19]	1.68 [19]	1.302 [2]*	0.618 [19]
<i>n</i> -Tetradecane	693 [19]	1.57 [19]	1.210 [2]*	0.654 [19]

Notes: The values marked by \* were obtained in the course of transition from one units (g/cm<sup>3</sup>) to another (mol/dm<sup>3</sup>). Original data [2] have three decimal digits.

“standard” *n*-alkane), one can assume that it will be valid for other *n*-alkanes when the reduced variables  $\tau \equiv T/T_c$ ,  $r \equiv (v_c/v)$  are used.

The procedure of obtaining the approximation for coefficient  $\lambda$  is as follows. As a “standard” *n*-alkane, *n*-butane has been chosen. For *n*-butane, the dependence of  $\lambda$  on density along two isotherms  $T = 450$  and  $550$  K has been obtained by solving a set of Eqs. (10) and (11) for several values of density taken from tabulated  $p$ – $v$ – $T$  data [17]. At each density value, we found such value of  $\lambda$  which resulted in the exact value of  $p$  shown in the table. The resultant isothermal dependencies of  $\lambda$  on  $\rho$  appeared to be close to linear. Approximating these dependencies by linear functions  $\lambda = a(T) + b(T)\rho$  along two isotherms  $T = 450$  and  $550$  K, and approximating coefficients  $a(T)$ ,  $b(T)$  by power functions of temperature, we have arrived at the following formula for the dimensionless parameter  $\lambda$ :

$$\lambda = 0.19381\tau^{-0.587} - 0.03734\tau^{-0.1753}r. \quad (15)$$

Taking into account Eq. (15), one can rewrite Eq. (14) in the form:

$$\bar{b} = a + dr, \quad (16)$$

where

$$a \equiv 0.19381\tau^{-0.587}Z_c^{-1}, \quad d \equiv -0.03734\tau^{-0.1753}Z_c^{-1}. \quad (17)$$

The last step in the derivation procedure—determination of two coefficients and two exponents in Eq. (15)—is completely of fitting nature. As the validity criterion of the EOS given by Eqs. (12) and (15) its prediction accuracy when compared with available data at densities  $\rho/\rho_c \leq 1$  and temperatures  $T \geq 273$  K is used for those *n*-alkanes and in those parametric domains where such data exist. The results of compar-

ison between predictions and available data are presented in Table 3.

It follows from Table 3 that our EOS provides the accuracy better than a fraction of percent almost everywhere at  $\rho < \rho_c$ . The maximum discrepancy between the predictions and experimental data is about 1% at pressures up to 10 MPa and about 1.5–2% at pressures from 10 to 20 MPa.

Table 4 shows the dependence of pressure on temperature along five curves  $\rho = \text{const}$  for *n*-octane and *n*-dodecane according to Eqs. (12)–(15). Contrary to Table 3, the data presented in Table 4 are the predictions as there are no experimental data available in literature on these *n*-alkanes (see Section 1.6 and Concluding Remarks).

### 1.3. Virial Equation of State for *n*-Alkanes

In approximation  $\lambda = \text{const}$ , Eq. (12) has a form of virial EOS. The corrected EOS taking into account the dependence of  $\lambda$  on density (see Eq. (15)) has originally a form different from the virial form. However, simple transformations allow obtaining the following equation exhibiting a virial form:

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3 + F\rho^4 + G\rho^5 + I\rho^6), \quad (18)$$

$$\Pi = r\tau/Z_c(1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3 + \bar{F}r^4 + \bar{G}r^5 + \bar{I}r^6), \quad (19)$$

where  $\bar{B}$ ,  $\bar{C}$ , ... are the dimensionless virial coefficients, defined as

$$\bar{B} \equiv B\rho_c, \quad \bar{C} \equiv C\rho_c^2, \quad \bar{D} \equiv D\rho_c^3, \dots \quad (20)$$

**Table 3.** Comparison of predicted pressure,  $p_a$ , given by the EOS of Eqs. (12), (15) with measured pressure,  $p$ , for various  $n$ -alkanes

Methane ( $T_c = 190.53$ K; $\rho_c = 10.150$ mol/dm <sup>3</sup> ; $p_c = 4.598$ MPa)				
Isobar $p = 4$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
186.089	5.379	4.070	4	1.8
270	1.976	3.999	4	0
300	1.716	3.999	4	0
400	1.223	3.999	4	0
Isobar $p = 5$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
270	2.537	5.000	5	0
300	2.181	5.000	5	0
350	1.792	4.999	5	0
400	1.534	5.001	5	0
Isobar $p = 10$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
280	5.328	10.00	10	0
300	4.685	9.994	10	0
350	3.695	9.989	10	0.1
400	3.101	9.988	10	0.1
500	2.389	9.991	10	0
600	1.963	10.00	10	0
Isobar $p = 20$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
400	6.142	19.71	20	1.5
450	5.280	19.78	20	1.1
500	4.659	19.83	20	0.9
600	3.807	19.90	20	0.5
Ethane ( $T_c = 305.34$ K; $\rho_c = 6.875$ mol/dm <sup>3</sup> ; $p_c = 4.8714$ MPa)				
Isobar $p = 3$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
282.908	2.072	3.030	3	1.0
300	1.659	3.007	3	0.23
350	1.207	3.006	3	0.20
400	0.9896	3.0076	3	0.25
Isobar $p = 4$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
295.98	3.227	4.040	4	1.0
300	2.827	4.020	4	0.5
350	1.718	4.007	4	0.18
400	1.364	4.0096	4	0.24
Isobar $p = 5$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
306.6	2.770	4.907	5	0.19
307	5.593	5.026	5	0.52
310	4.152	5.045	5	0.9
350	2.313	5.009	5	0.18
400	1.764	5.012	5	0.24
450	1.471	5.011	5	0.22



Table 3. (Contd.)

Isobar $p = 6$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
320	5.325	6.086	6	1.4
350	3.023	6.020	6	0.3
400	2.191	6.013	6	0.2
450	1.799	6.015	6	0.25
Isobar $p = 10$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
354	6.840	10.10	10	1.0
370	5.481	10.14	10	1.4
385	4.703	10.09	10	0.9
400	4.182	10.06	10	0.6
450	3.204	10.02	10	0.2
500	2.677	10.01	10	0.1
600	2.076	10.009	10	0.09
Isobar $p = 20$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
500	5.490	19.66	20	1.7
550	4.685	19.74	20	1.3
600	4.121	19.78	20	1.1
Propane ( $T_c = 369.85$ K; $\rho_c = 5.0$ mol/dm <sup>3</sup> ; $p_c = 4.2477$ MPa)				
Isobar $p = 3$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
350.819	1.787	2.999	3	0
270	1.976	3.0027	3	0
Isobar $p = 4.4$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
374	3.393	4.407	4.4	0.16
380	2.690	4.414	4.4	0.32
400	2.018	4.408	4.4	0.2
450	1.469	4.405	4.4	0.11
Isobar $p = 6$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
392	5.021	5.998	6	0
396	4.379	6.071	6	1.2
400	3.905	6.080	6	1.3
450	2.211	6.018	6	0.3
500	1.743	6.0068	6	0.11
Isobar $p = 10$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
441	5.092	10.029	10	0.3
460	4.222	10.104	10	1
500	3.241	10.034	10	0.34
600	2.242	9.964	10	0.36
Isobar $p = 14$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
500	4.751	13.83	14	1.2
520	4.292	13.88	14	0.9
550	3.772	13.89	14	0.8
600	3.183	13.86	14	1.0

**Table 3.** (Contd.)

<i>n</i> -Butane ( $T_c = 425.16$ K; $\rho_c = 3.920$ mol/dm <sup>3</sup> ; $p_c = 3.796$ MPa)				
Isobar $p = 3.85$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
428	2.593	3.828	3.85	0.58
440	1.874	3.856	3.85	0.16
500	1.190	3.849	3.85	0
Isobar $p = 5$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
450	3.145	5.031	5	0.62
500	1.708	5.015	5	0.30
600	1.151	4.998	5	0
Isobar $p = 10$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
520	3.957	5.998	10	0
550	3.245	6.071	10	0.7
600	2.561	6.080	10	0.3
Isobar $p = 12$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
570	3.570	11.95	12	0.41
580	3.405	11.96	12	0.33
590	3.258	11.97	12	0.25
600	3.126	11.97	12	0.25
<i>n</i> -Hexane ( $T_c = 507.37$ K; $\rho_c = 2.7109$ mol/dm <sup>3</sup> ; $p_c = 3.046$ MPa)				
Isobar $p = 3.2$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
520	1.517	3.197	3.2	0.09
550	1.061	3.204	3.2	0.13
600	0.8201	3.201	3.2	0.03
Isobar $p = 4$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
530	2.526	4.010	4	0.25
550	1.619	4.032	4	0.79
600	1.106	4.008	4	0.19
630	0.9741	4.0025	4	0.06
Isobar $p = 5$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
580	1.792	5.083	5	1.7
600	1.532	6.071	5	0.98
630	1.3016	6.080	5	0.40
Isobar $p = 6$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_a$ , MPa	$p$ , MPa	$ p_a - p /p$ , %
600	2.029	6.143	6	1.17
610	1.883	6.1115	6	1.92
630	1.666	6.070	6	2.38

**Table 4.** Predicted dependence of pressure on temperature along five curves  $\rho = \text{const}$ 

<i>n</i> -Octane ( $T_c = 568.7 \text{ K}$ ; $p_c = 2.49 \text{ MPa}$ ; $\rho_c = 2.20 \text{ mol/dm}^3$ )					
$T, \text{ K}$	$\rho/\rho_c = 0.1$	$\rho/\rho_c = 0.2$	$\rho/\rho_c = 0.3$	$\rho/\rho_c = 0.4$	$\rho/\rho_c = 0.5$
	$p, \text{ MPa}$				
500	0.7346	1.1404	1.2677	1.1687	0.8950
600	0.9646	1.6927	2.2305	2.6243	2.9190
700	1.1801	2.1873	3.0644	3.8535	4.5936
800	1.3884	2.6536	3.8357	4.9732	6.1010
1000	1.7947	3.5450	5.2872	7.0544	8.8750
1200	2.1943	4.4102	6.6811	9.0360	11.499
1500	2.7883	5.6870	8.7266	11.931	15.320
2000	3.7726	7.7930	12.088	16.677	21.572
2500	4.7543	9.8890	15.428	21.388	27.777
3000	5.7349	11.982	18.761	26.087	33.966

<i>n</i> -Dodecane ( $T_c = 658 \text{ K}$ ; $p_c = 1.82 \text{ MPa}$ ; $\rho_c = 1.3914 \text{ mol/dm}^3$ )					
$T, \text{ K}$	$\rho/\rho_c = 0.1$	$\rho/\rho_c = 0.2$	$\rho/\rho_c = 0.3$	$\rho/\rho_c = 0.4$	$\rho/\rho_c = 0.5$
	$p, \text{ MPa}$				
500	0.3925	0.4373	0.1741	—	—
600	0.5642	0.8911	1.0170	0.9794	0.8150
700	0.7138	1.2571	1.6636	1.9671	2.2001
800	0.8536	1.5840	2.2228	2.9010	3.3477
1000	1.1196	2.1839	3.2210	4.2583	5.3190
1200	1.3773	2.7508	4.1464	5.588	7.0957
1500	1.7574	3.5758	5.4786	7.486	9.6145
2000	2.3844	4.9250	7.6433	10.555	13.671
2500	3.0085	6.2638	9.7842	13.583	17.670
3000	3.6315	7.5983	11.917	16.600	21.652

According to Eqs. (7) and (20), the dimensionless second virial coefficient can be presented in the form:

$$\bar{B} \equiv (\rho_c R T_c / p_c) [f_0 + \omega f_1] \quad (21)$$

with the functions of the reduced temperature,  $\tau$ , given by Eqs. (8) and (9).

Other dimensionless virial coefficients can be expressed in terms of parameters  $a$  and  $d$  (see Eq. (17)) as:

$$\begin{aligned} \bar{C} &= a^2, \quad \bar{D} = a^3 + 2ad, \quad \bar{F} = 3a^2d + d^2, \\ \bar{G} &= 3ad^2, \quad \bar{I} = d^3. \end{aligned} \quad (22)$$

Equation (19) with coefficients given by Eqs. (21), (22) is equivalent to Eqs. (12)–(15).

It is worth noting that Eq. (19) is one of approximations of the EOS in the form of virial series with the finite number of terms. All coefficients in this equation except two first coefficients (1 and  $B$ ) are not true virial coefficients. Five coefficients in Eq. (22), from  $\bar{C}$  to  $\bar{I}$  contain four common fitting parameters: two coefficients and two exponents in Eqs. (17) for  $a$  and  $d$ .

#### 1.4. First and Second Derivatives of Virial Coefficients for *n*-Alkanes

For calculating internal energy, the first derivatives of virial coefficients are required (see (Eqs. (4) and (5))) whereas for calculating specific heats, the second derivatives of virial coefficients are required. Both first and

second derivatives of virial coefficients can be obtained by differentiating formulae (22) with regard for temperature dependencies of coefficients  $a$  and  $d$  (see Eqs. (17)). The results of calculations are presented below.

### First Derivatives

$$f_{01} = \tau \frac{df_0}{d\tau} = \frac{0.33}{\tau} + \frac{0.2770}{\tau^2} + \frac{3.63 \times 10^{-2}}{\tau^3} + \frac{4.856 \times 10^{-3}}{\tau^8}, \quad (23)$$

$$f_{11} = \tau \frac{df_1}{d\tau} = -\frac{0.662}{\tau^2} + \frac{1.269}{\tau^3} + \frac{6.4 \times 10^{-2}}{\tau^8},$$

$$\bar{B}_1 = \tau \frac{d\bar{B}}{d\tau} = \frac{\rho_c R T_c}{p_c} (f_{01} + \omega f_{11}), \quad (24)$$

$$\bar{C}_1 = \tau \frac{d\bar{C}}{d\tau} = -1.174a^2,$$

$$\bar{D}_1 = \tau \frac{d\bar{D}}{d\tau} = -(1.5246ad + 1.761a^3),$$

$$\bar{F}_1 = \tau \frac{d\bar{F}}{d\tau} = -(0.3506d^2 + 4.0479a^2d), \quad (25)$$

$$\bar{G}_1 = \tau \frac{d\bar{G}}{d\tau} = -2.8125ad^2,$$

$$\bar{I}_1 = \tau \frac{d\bar{I}}{d\tau} = -0.5259d^3.$$

### Second Derivatives

$$f_{02} = \tau \frac{df_{01}}{d\tau} = -\frac{0.2770}{\tau^2} - \frac{7.26 \times 10^{-2}}{\tau^3} - \frac{3.3992 \times 10^{-2}}{\tau^8}, \quad (26)$$

$$f_{12} = \tau \frac{df_{11}}{d\tau} = \frac{0.662}{\tau^2} - \frac{2.538}{\tau^3} - \frac{0.448}{\tau^8},$$

$$\bar{B}_{2t} = \frac{d(\tau \bar{B}_1)}{d\tau} = \frac{\rho_c R T_c}{p_c} (f_{02} + \omega f_{12}), \quad (27)$$

$$\bar{C}_{2t} = \frac{d(\tau \bar{C}_1)}{d\tau} = 0.20428a^2,$$

$$\bar{D}_{2t} = \frac{d(\tau \bar{D}_1)}{d\tau} = -0.3624ad + 1.34717a^3,$$

$$\bar{F}_{2t} = \frac{d(\tau \bar{F}_1)}{d\tau} = -0.22768d^2 + 1.41693a^2d, \quad (28)$$

$$\bar{G}_{2t} = \frac{d(\tau \bar{G}_1)}{d\tau} = -0.17552ad^2,$$

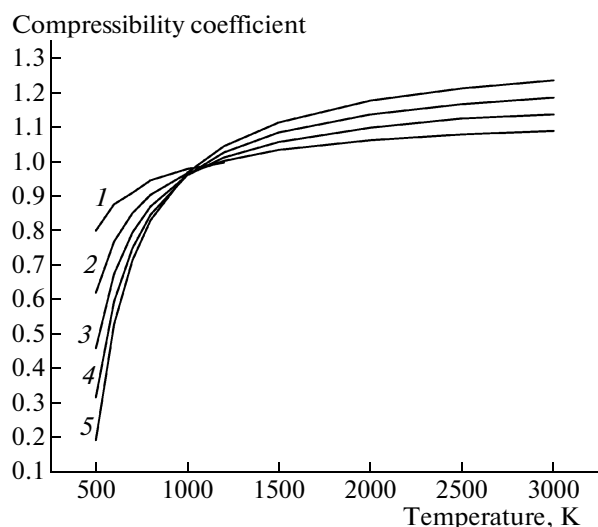
$$\bar{I}_{2t} = \frac{d(\tau \bar{I}_1)}{d\tau} = -0.24933d^3.$$

### 1.5. On the Calculation of Density or Temperature Based on Other Two Variables of the Thermal Equation of State

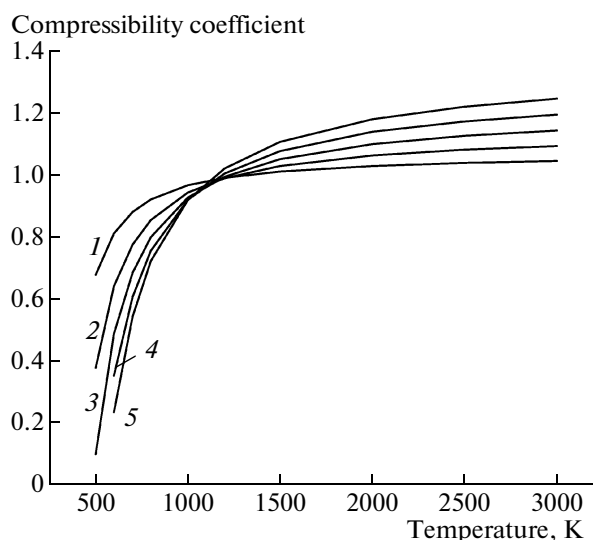
The EOS (12)–(15) provides explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively. The commands of the “ROOT” type available in commercial mathematical packages allow obtaining the result nearly instantaneously if the initial approximation  $X_0$  of the solution (“guess”) is close to the solution  $X_s$ . When dealing with CFD problems, it is sufficient to use the value of  $X_s$  in the neighbouring computational node as a guess  $X_0$  in the node of interest.

When applied to temperatures exceeding 600–700 K, all existing EOS for  $n$ -alkanes containing parameters determined from experimental  $p$ – $\rho$ – $T$  data have to be considered as extrapolations. Limitation of available systematic experimental  $p$ – $\rho$ – $T$  data with temperatures of 600–700 K is not occasional. At temperatures exceeding this limit but less than 1100–1500 K, reactions of monomolecular decomposition are hardly possible, however, qualitative transformations of intermolecular motion come into play (except for methane and ethane). Moreover, in dense gases where the characteristic number of molecular collisions is high, essential role can be played by bimolecular and other chemical reactions. In view of it, the dependence between  $p$ – $\rho$ – $T$  variables becomes time dependent to a certain degree or, in other words, becomes thermodynamically nonequilibrium. The use of thermodynamic functions under such conditions becomes less justified and should be treated as approximation. In these conditions, when dealing with CFD calculations, the main demand to the EOS appears to be the correlation between thermal and calorific variables rather than high accuracy of  $p$ – $v$ – $T$  data (the latter cannot be attained in principle). Such correlation is obtained by using one and the same thermal EOS for both approximating  $p$ – $v$ – $T$  data and calculating excessive thermodynamic functions. The accuracy of such correlation is also ensured by analytical differentiation of virial coefficients (see Section 1.4) and analytical integration (see Section 1.9).

The other general demand to the high-temperature asymptotic of EOS is that along the isochoric curve (at low densities) the compressibility coefficient should cross a unity value (Boyle point) with further increase, which slows down gradually with temperature and attains a maximum value. After passing the maximum, at temperatures  $T \gg T_c$ , the compressibility coefficient must approach the unity value again which indicates that  $p$ – $v$ – $T$  dependence tends asymptotically to the ideal gas law. The latter condition is not strict as it is related to very high temperatures (several thousand



**Fig. 2.** Predicted evolution of compressibility coefficient for *n*-octane along isochoric curves  $\rho/\rho_c = 0.1$  (curve 1), 0.2 (2), 0.3 (3), 0.4 (4), and 0.5 (5).



**Fig. 3.** Predicted evolution of compressibility coefficient for *n*-dodecane along isochoric curves  $\rho/\rho_c = 0.1$  (curve 1), 0.2 (2), 0.3 (3), 0.4 (4), and 0.5 (5).

Kelvin). Figures 2 and 3 show the results of calculations of the compressibility coefficient

$$Z = 1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3 + \bar{F}r^4 + \bar{G}r^5 + \bar{I}r^6$$

along several isochoric curves for *n*-octane and *n*-dodecane. Clearly, thermal EOS meets the requirements mentioned above.

#### 1.6. Liquid–Vapour Phase Equilibrium Curves for *n*-Alkanes

There exist a number of approximations of liquid–vapor phase equilibrium curves  $p(T)$  (see, e.g., Dodge [20]) that contain from two to four fitting parameters. The most physically grounded approximation of  $p(T)$ -curve starting from the triple point to the critical point for *n*-alkanes from  $C_5$  to  $C_{20}$  is that suggested by Ruzicka and Majer [19] based on the Cox formula:

$$\ln(p/p_0) = (1 - T_0/T) \exp(A_0 + A_1 T + A_2 T^2). \quad (29)$$

In Eq. (29), the normal boiling point ( $T_0 = T_b, p_0 = 0.101325$  MPa) is taken as a reference state ( $p_0, T_0$ ). The values of parameters entering Eq. (29) for *n*-alkanes from *n*-pentane to *n*-tetradecane are presented in Table 5.

For four light *n*-alkanes, from methane to *n*-butane, the approximation of the  $p(T)$ -curve with six fitting parameters has been obtained, which include the data on the triple point  $p_t, T_t$  [17]. This approximation has the form:

$$\begin{aligned} \ln(p/p_t) \\ = A_1 x + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x(1-x)^{A_6}, \end{aligned} \quad (30)$$

where<sup>1</sup>

$$x = (1 - T_t/T)/(1 - T_t/T_c)$$

and  $T_t$  is the triple point temperature. The values of parameters  $A_1, \dots, A_6$  entering Eq. (30) are presented in Table 6.

In CFD applications, only high-temperature part of the  $p(T)$ -curve is usually of most interest. For *n*-alkanes from  $C_1$  to  $C_6$  at temperature  $\geq 100^\circ\text{C}$  and from  $C_8$  to  $C_{14}$  at temperature  $\geq 160^\circ\text{C}$ , the experimental data on the  $p(T)$ -curve (including the critical point) are reproduced with the accuracy of tenth and hundredth fraction of percent by the two-parameter approximation [21]:

$$p = [(T/\alpha)^{1/8} - A]^8. \quad (31)$$

Equation (31) allows obtaining the analytical form of the dependence  $T = T(p)$  along the  $p(T)$ -curve. Values of parameters  $\alpha$  and  $A$  in Eq. (31) are presented in Table 7.

#### 1.7. Ideal-Gas Specific Heats and Thermodynamic Functions for *n*-Alkanes

In the literature on thermophysical properties of multiatomic gases, specific heat,  $C_p$ , in the ideal-gas state,  $C_{p0}$ , is usually represented either in the form of temperature polynomials or in the form of other approximations containing exponential functions of the form  $\exp(-A_i/T)$ , where  $A_i$  are the positive constants. The latter resemble some formulae of statistical physics for the specific heat of harmonic oscillators.

<sup>1</sup> In the original paper [17], there is a misprint in the formula for  $x$  (Eq. (3) [17]): the nominator in the right hand side of the formula is denoted as  $1 - T_c/T$  instead of the correct expression  $1 - T_t/T$ .

**Table 5.** Parameters of Eq. (29) for *n*-alkanes from *n*-pentane to *n*-tetradecane

<i>n</i> -Alkane	$A_0$	$A_1$	$A_2$	$T_0$ , K	$p_0$ , kPa
<i>n</i> -Pentane	2.73425	−1.966544E−3	2.408406E−6	309.209	101.325
<i>n</i> -Hexane	2.79797	−2.022083E−3	2.287564E−6	341.863	101.325
<i>n</i> -Heptane	2.86470	−2.113204E−3	2.250991E−6	371.552	101.325
<i>n</i> -Octane	2.90150	−2.046204E−3	2.010759E−6	398.793	101.325
<i>n</i> -Nonane	2.94690	−2.051933E−3	1.903683E−6	423.932	101.325
<i>n</i> -Decane	2.96690	−1.932579E−3	1.644626E−6	447.269	101.325
<i>n</i> -Undecane	3.02711	−2.045579E−3	1.712658E−6	469.042	101.325
<i>n</i> -Dodecane	3.05854	−2.018454E−3	1.606849E−6	489.438	101.325
<i>n</i> -Tridecane	3.10403	−2.071819E−3	1.611600E−6	508.602	101.325
<i>n</i> -Tetradecane	3.13624	−2.063853E−3	1.541507E−6	526.691	101.325

**Table 6.** Parameters of Eq. (30) for *n*-alkanes from methane to *n*-butane

<i>n</i> -Alkane	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$
Methane	4.77939953	1.757393941	−0.566507391	0.0	1.326326855	1.5
Ethane	8.900377023	11.559508931	−4.009244950	−1.175263997	7.918066027	1.6
Propane	15.410153272	11.870733615	−0.874958355	−2.448971934	11.400962259	1.2
<i>n</i> -Butane	−7.645674906	24.578459427	−1.096617182	−0.289083373	25.161929277	1.03

From now on, for the sake of brevity such approximations will be referred to as “exponential” approximations to differ them from the “polynomial” ones. The aim of the approximations is to represent precisely the experimental data on the specific heat for gases that are sufficiently rarefied to be treated as the ideal gas.

The approximation formulae for *n*-alkanes have been reported in [22, 23]. Bibliography on previous works is published elsewhere [23]. The polynomials of [23] have the form:

$$C_{p0} = a_1 + a_2 T + a_3 T^2 + a_4 T^3. \quad (32)$$

The parameters of Eq. (32) are determined in [23] based on the API data [24]. Table 8 shows the corresponding parameters for *n*-alkanes from C<sub>1</sub> to C<sub>14</sub> taken from [23]. Note that the original paper [23] contains a misprint: the heading of the sixth column should read  $a_4 \times 10^9$  rather than  $a_4 \times 10$ .

Integration of Eq. (32) gives the enthalpy (with zero value at  $T = 0$ ):

$$H_0 = a_1 T + a_2 T^2/2 + a_3 T^3/3 + a_4 T^4/4 \quad (33)$$

and the entropy (with a certain reference value of temperature, for example,  $T_0 = 298.15$  K):

$$S_0 = \int_{T_0}^T \frac{C_{p0}}{T} dT = a_1 \ln T + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \text{const}(T_0). \quad (34)$$

The polynomial approximation agrees well with the smoothened experimental data (within a fraction of 0.1 to 0.01 of experimental accuracy equal approximately to 1%). The other advantage of the polynomial approximation is that it is readily integrated analytically. This fact simplifies calculations of enthalpy and

**Table 7.** Parameters  $\alpha_n$  and  $A_n$  calculated based on the experimental data [2] on the liquid–vapor phase equilibrium curves for *n*-alkanes from methane ( $n = 1$ ) to eicosane ( $n = 20$ )

<i>n</i>	1	2	3	4	5	6	7	8	9	10
$\alpha_n \times 10^6$	3.30128	3.03053	3.04209	2.96285	2.96957	2.5841	2.40418	2.16091	1.97704	1.8331
$A_n$	7.72428	8.42164	8.65162	8.88897	9.04352	9.35207	9.55656	9.79516	9.99946	10.1789
<i>n</i>	11	12	13	14	15	16	17	18	19	20
$\alpha_n \times 10^6$	1.5433	1.4708	1.3762	1.3276	1.2796	1.16201	1.1525	1.1542	1.1292	1.0839
$A_n$	10.491	10.6219	10.7752	10.8801	10.9829	11.172	11.2283	11.2639	11.3342	11.4319

**Table 8.** Constants for four-term polynomial Eq. (32) for the specific heat,  $C_{p0}$ , of *n*-alkanes

<i>n</i> -Alkane	$a_1 \times 10$	$a_2 \times 10^2$	$a_3 \times 10^6$	$a_4 \times 10^9$	Temperature range, K	Error	
						avg., %	400 K: max %
Methane	45.9765	1.24471	2.8597	−2.7031	298.16–1500	0.52	1.44
Ethane	12.9285	4.25354	−16.5699	2.08148	298.16–1500	0.18	0.7
Propane	−10.08568	7.31499	−37.8885	7.67782	298.16–1500	0.09	0.28
<i>n</i> -Butane	−5.85433	9.35864	−48.4829	9.74318	298.16–1500	0.09	0.39
<i>n</i> -Pentane	−8.66195	11.6434	−61.6297	12.6705	298.16–1500	0.10	0.35
<i>n</i> -Hexane	−10.5432	13.899	−74.4861	15.5057	298.16–1500	0.10	0.34
<i>n</i> -Heptane	−12.2928	16.1454	−87.2008	18.2892	298.16–1500	0.10	0.30
<i>n</i> -Octane	−14.5557	18.4159	−100.202	21.15	298.16–1500	0.09	0.30
<i>n</i> -Nonane	−16.6454	20.6822	−113.266	24.0958	298.16–1500	0.10	0.29
<i>n</i> -Decane	−18.9006	22.9539	−126.325	27.011	298.16–1500	0.10	0.28
<i>n</i> -Undecane	−20.0474	25.1665	−138.506	29.5438	298.16–1500	0.10	0.27
<i>n</i> -Dodecane	−22.2751	27.4378	−151.569	32.4628	298.16–1500	0.10	0.26
<i>n</i> -Tridecane	−24.9852	29.7363	−165.084	35.5837	298.16–1500	0.10	0.26
<i>n</i> -Tetradecane	−26.2339	31.9544	−177.354	38.1652	298.16–1500	0.10	0.25

**Table 9.** Constants of “exponential” approximation (35) for the specific heat,  $C_{p0}$ , of *n*-alkanes

<i>n</i> -Alkane	$\alpha$	$\beta$	$\gamma$	$n$	Temperature range, K	Error	
						avg., %	1500 K: max %
Methane	7.8234	22.2871	2295.4564	1.1411	298.16–1500	0.06	0.17
Ethane	9.2796	41.7753	862.2394	1.0230	298.16–1500	0.09	0.23
Propane	9.9953	64.3116	401.2782	0.9187	298.16–1500	0.04	0.09
<i>n</i> -Butane	15.0558	74.3464	726.7993	1.018	298.16–1500	0.06	0.16
<i>n</i> -Pentane	18.3962	90.2419	733.3930	1.0223	298.16–1500	0.06	0.16
<i>n</i> -Hexane	21.9241	105.7232	760.7426	1.0298	298.16–1500	0.06	0.15
<i>n</i> -Heptane	25.3038	121.7757	756.6982	1.0302	298.16–1500	0.07	0.15
<i>n</i> -Octane	28.8706	136.8702	788.7739	1.0380	298.16–1500	0.06	0.16
<i>n</i> -Nonane	32.1577	153.2757	768.9929	1.0346	298.16–1500	0.06	0.15
<i>n</i> -Decane	35.5614	169.1588	770.4296	1.0356	298.16–1500	0.05	0.14
<i>n</i> -Undecane	39.1996	184.1528	798.8245	1.0420	298.16–1500	0.07	0.16
<i>n</i> -Dodecane	42.5522	200.2045	792.4845	1.0411	298.16–1500	0.06	0.14
<i>n</i> -Tridecane	45.8009	216.6082	776.8577	1.0383	298.16–1500	0.06	0.13
<i>n</i> -Tetradecane	49.3789	231.9104	792.4828	1.0418	298.16–1500	0.06	0.16

internal energy. However, the essential drawback of polynomial approximations is that they are valid only within a certain temperature range. The use of polynomial approximations beyond this range can result in large deviations from the true values of the specific heat.

When deriving analytical approximations for the specific heat that cover a wide range of temperature, it is desirable that, on the one hand, they agree with experimental data available in a certain range of temperature and, on the other hand, they exhibit a physically grounded asymptotic behavior in the low-tem-

**Table 10.** Constants of approximation (38) for calculating ideal-gas specific heat,  $C_{p0}$ , of different  $n$ -alkanes

$n$ -Alkane	$A$	$B_1$	$C_1$	$B_2$	$C_2$
$n$ -Pentane	86.389058	163.62772	1404.5312	125.55904	3247.1465
$n$ -Hexane	101.85997	196.40919	1400.5301	137.69426	3214.2702
$n$ -Heptane	117.22475	151.73507	3154.9913	227.31996	1391.9171
$n$ -Octane	132.49098	166.06550	3048.8270	254.85474	1378.6073
$n$ -Nonane	148.15036	288.24904	1380.8003	178.57491	3051.1566
$n$ -Decane	163.73837	320.24325	1379.9706	191.23849	3024.7636
$n$ -Undecane	179.21063	350.72479	1376.4867	205.11522	2988.5224
$n$ -Dodecane	194.67625	219.19909	2956.5645	381.04958	1373.3800
$n$ -Tridecane	210.13549	411.22701	1370.5730	233.46990	2928.1171
$n$ -Tetradecane	225.58955	247.90156	2902.6832	441.27841	1368.0279

perature and high-temperature limits. Such properties are pertinent to “exponential” approximations. One of known approximations of this type is the four-parameter “exponential” approximation:

$$C_{p0} = \alpha + \beta \exp(-\gamma/T^n). \quad (35)$$

The parameters in Eq. (35) for  $n$ -alkanes have been determined in [25] based on the API data [24]. Table 9 shows the values of these parameters for  $n$ -alkanes from  $C_1$  to  $C_{14}$  taken from [25].

The accuracy of Eq. (35) with parameters of Table 9 [25] is as high as that of Eq. (32) and is sufficient for approximating available experimental data. The main drawback of Eq. (35) is that it cannot be integrated analytically. However this drawback is not critical as the exponential function of Eq. (35) can be integrated numerically very fast in one of commercially available mathematical packages. The approximation of Eq. (35) with the parameters shown in Table 9 can be reliably applied at temperatures  $T \leq 1500$  K.

Qualitatively correct high-temperature asymptotic of Eq. (35) makes it possible to apply it for temperatures  $T > 1500$  K in approximate calculations. A more precise calculation of the specific heat in CFD problems is hardly required without simultaneous account for chemical processes of thermal destruction, etc., relevant to hydrocarbons at temperatures  $T > 1500$  K. When using the approximation of Eq. (35), the enthalpy,  $H_0$ , can be found numerically from the relationship:

$$H_0 = \alpha T + \beta \int_0^T \exp\left(-\frac{\gamma}{\xi^n}\right) d\xi \quad (36)$$

(with zero value at  $T = 0$ ). The entropy can also be found numerically from the relationship

$$S_0 = \alpha \ln T + \beta \int_{T_0}^T \exp\left(-\frac{\gamma}{\xi^n}\right) \frac{d\xi}{\xi}. \quad (37)$$

In addition to the approximations presented by Eqs. (32) and (35), there exist other approximations for the specific heat. Worth noting is the five-parameter approximation [19, 26] which is based on representing molecular oscillators by two groups of harmonic oscillators. Such an approximation is valid within the temperature range  $200 \text{ K} \leq T \leq 1000 \text{ K}$  and is given by the formula:

$$C_{p0} = A + \sum_{i=1}^2 B_i \frac{(C_i/T)^2 \exp(-C_i/T)}{[1 - \exp(-C_i/T)]^2}. \quad (38)$$

Parameters of Eq. (38) for  $n$ -alkanes from  $C_5$  to  $C_{14}$  have been obtained in [26] based on TRC tables [27]. These parameters are shown in Table 10.

At  $T \leq 1000$  K, the approximation of Eq. (38) agrees with the approximations of Eqs. (32) and (35) within a fraction of percent.

Equation (38) has the form of the temperature derivative of enthalpy,  $H_0$ , of a molecule with two corresponding groups of harmonic oscillators:

$$H_0 = AT + \sum_{i=1}^2 \frac{B_i C_i}{\exp(C_i/T) - 1}. \quad (39)$$

When solving CFD problems which do not require the use of data for lower alkanes (up to  $n$ -butane) and the demands for high accuracy of calculations are related to temperatures less than 1000 K, the approximation of Eq. (38) is more preferable than that of Eq. (35) due to existence of the precise relation for enthalpy (Eq. (39)).

Specific heats  $C_{p0}$  and  $C_{v0}$  are related to each other via the well-known thermodynamic relationships

$$C_{v0} = C_{p0} - R \quad (40)$$

(for molar specific heats) and

$$C_{v0} = C_{p0} - R_g \quad (41)$$

(for mass specific heats), where  $R$  is the universal gas constant,  $R_g = R/\mu$  is the gas constant, and  $\mu$  is the molecular mass. If the specific heat in Eqs. (32), (35),



and (38) is taken in J/(mol K), the following formulae can be derived for  $C_{v0}$ :

$$C_{v0} = a_1 - 8.3143 + a_2 T + a_3 T^2 - a_4 T^3 \text{ J/(mol K)}, \quad (42)$$

$$C_{v0} = \alpha - 8.3143 + \beta \exp(-\gamma/T^n) \text{ J/(mol K)}, \quad (43)$$

$$C_{v0} = A - 8.3143 + \sum_{i=1}^2 B_i \frac{(C_i/T)^2 \exp(-C_i/T)}{[1 - \exp(-C_i/T)]^2} \text{ J/(mol K)}. \quad (44)$$

These three approximations for  $C_{v0}$  result in the corresponding approximations for the internal energy,  $E_0$ :

$$E_0 = (a_1 - 8.3143)T + a_2 T^2/2 \quad (45)$$

$$+ a_3 T^3/3 + a_4 T^4/4 \text{ J/(mol K)},$$

$$E_0 = (\alpha - 8.3143)T + \beta \int_0^T \exp(-\gamma/T^n) dT \text{ J/(mol K)}, \quad (46)$$

$$E_0 = (A - 8.3143)T + \sum_{i=1}^2 \frac{B_i C_i}{\exp(C_i/T) - 1} \text{ J/(mol K)}. \quad (47)$$

### 1.8. Excess Thermodynamic Functions and Excess Specific Heats for *n*-Alkanes

If the thermal EOS is specified in the form of the relationship between three variables— $p$ ,  $T$ , and  $\rho$ —then the excess internal energy  $E_{exc}(T, \rho)$  can be determined based on the known thermodynamic relationship:

$$E_{exc}(T, \rho) = - \int_0^\rho [T(\partial p / \partial T)_\rho - p] d\rho / \rho^2. \quad (48)$$

Substitution of the EOS (19) in the integral function of Eq. (48) results in a virial series which is similar to Eq. (19). In this series, all virial coefficients  $\bar{B}$ ,  $\bar{C}$ , ..., and  $\bar{I}$  are replaced by the corresponding logarithmic derivatives with respect to temperature:  $\tau d\bar{B}/d\tau$ ,  $\tau d\bar{C}/d\tau$ , ..., and  $\tau d\bar{I}/d\tau$ . The final expression for  $E_{exc}(T, \rho)$  is obtained by integration of the virial series with respect to  $\rho$ . Omitting the details, we present here the final result:

$$E_{exc}/(RT) = -(\bar{B}_1 r + \bar{C}_1 r^2/2 + \bar{D}_1 r^3/3 + \bar{F}_1 r^4/4 + \bar{G}_1 r^5/5 + \bar{I}_1 r^6/6), \quad (49)$$

where index 1 denotes the corresponding logarithmic derivatives:  $\bar{B}_1 = \tau d\bar{B}/d\tau$ ,  $\bar{C}_1 = \tau d\bar{C}/d\tau$ , etc. (Section 1.4).

Differentiation of Eq. (49) with respect to temperature results in the following relationship for the excess specific heat at constant volume,  $C_{v, exc}$ :

$$\frac{C_{v, exc}}{R} = -\left(\bar{B}_{2t} r + \frac{\bar{C}_{2t} r^2}{2} + \frac{\bar{D}_{2t} r^3}{3} + \frac{\bar{F}_{2t} r^4}{4} + \frac{\bar{G}_{2t} r^5}{5} + \frac{\bar{I}_{2t} r^6}{6}\right), \quad (50)$$

where index 2 denotes the corresponding derivatives of virial coefficients:  $\bar{B}_{2t} \equiv d(\tau \bar{B}_1)/d\tau$ ,  $\bar{C}_{2t} \equiv d(\tau \bar{C}_1)/d\tau$ , etc. (Section 1.4).

The excess enthalpy can be calculated based on the excess internal energy and excess pressure:

$$H_{exc} = E_{exc} + p_{exc}/\rho, \quad (51)$$

where

$$p_{exc}/(\rho RT) = (p - p_{id})/(\rho RT) = \bar{B}r + \bar{C}r^2 + \bar{D}r^3 + \bar{F}r^4 + \bar{G}r^5 + \bar{I}r^6 \quad (52)$$

and  $p_{id}$  is the ideal-gas pressure.

Differentiation of Eq. (51) with respect to temperature and using Eq. (52) results in the following relationship for the excess specific heat at constant pressure,  $C_{p, exc}$ :

$$C_{p, exc}/R = C_{v, exc}/R + \bar{B}_s r + \bar{C}_s r^2 + \bar{D}_s r^3 + \bar{F}_s r^4 + \bar{G}_s r^5 + \bar{I}_s r^6, \quad (53)$$

where index  $s$  means that the corresponding virial coefficient ( $A_i = \bar{B}, \bar{C}, \dots, \bar{G}$ ) is replaced with the derivative of  $\tau A_i$  with respect to  $\tau$ , i.e.,

$$\bar{B}_s \equiv d(\tau \bar{B})/d\tau \equiv \bar{B} + \bar{B}_1, \dots, \bar{I}_s \equiv d(\tau \bar{I})/d\tau \equiv \bar{I} + \bar{I}_1. \quad (54)$$

All formulae for calculating dimensionless virial coefficients and their derivatives  $\bar{B}_1$ ,  $\bar{C}_1$ , ..., are presented in Sections 1.3 and 1.4.

The excess entropy can be calculated using the thermal  $p$ - $\rho$ - $T$  EOS as follows:

$$S_{exc} = S - S_0 = -R \ln \left( \frac{\rho RT}{p_0} \right) + \int_0^\rho [\rho R - (\partial p / \partial T)_\rho] d\rho / \rho^2, \quad (55)$$

where  $S_0$  is the ideal-gas entropy determined in Section 1.7,  $p_0$  is the pressure in standard conditions (usually,  $p_0 = 1 \text{ atm} = 0.101325 \text{ MPa}$ ).

Substituting EOS (19) in the integral of Eq. (55) gives the following result:

$$\int_0^p [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \quad (56)$$

$$= -R \int_0^r (\bar{B}_s + \bar{C}_s r + \bar{D}_s r^2 + \bar{F}_s r^3 + \bar{G}_s r^4 + \bar{I}_s r^5) dr,$$

where parameters with index  $s$  are defined by Eqs. (54). The integral in the right-hand-side of Eq. (56) can be found analytically. Substituting the result of integration to Eq. (55) gives finally:

$$\frac{S_{exc}}{R} = -\ln\left(\frac{\rho RT}{0.101325}\right) - (\bar{B}_s r + \bar{C}_s r^2 / 2 + \bar{D}_s r^3 / 3 + \bar{F}_s r^4 / 4 + \bar{G}_s r^5 / 5 + \bar{I}_s r^6 / 6), \quad (57)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434$  kJ/(mol K).

### 1.9. Thermodynamic Functions and Specific Heats for $n$ -Alkanes

The internal energy as a function of two variables—temperature  $T$  and density  $\rho$ —can be calculated now as a sum of the ideal-gas internal energy  $E_0$  and the excess internal energy  $E_{exc}$ :

$$E(T, \rho) = E_0(T) + E_{exc}(T, \rho). \quad (58)$$

The enthalpy as a function of two variables—temperature  $T$  and density  $\rho$ —can be calculated as a sum of the ideal-gas enthalpy  $H_0$  and the excess enthalpy  $H_{exc}$ :

$$H(T, \rho) = H_0(T) + H_{exc}(T, \rho). \quad (59)$$

The specific heat at constant volume,  $C_v$ , as a function of two variables—temperature  $T$  and density  $\rho$ —can be calculated as sum of the ideal-gas specific heat at constant volume  $C_{v0}$  and the excess specific heat at constant volume  $C_{v, exc}$ :

$$C_v = C_{v,0} + C_{v, exc}. \quad (60)$$

The specific heat at constant pressure,  $C_p$ , as a function of two variables—temperature  $T$  and density  $\rho$ —can be calculated as a sum of the ideal-gas specific heat at constant pressure  $C_{p0}$  and excess specific heat at constant pressure  $C_{p, exc}$ :

$$C_p = C_{p,0} + C_{p, exc}. \quad (61)$$

The entropy as a function of two variables—temperature  $T$  and density  $\rho$ —can be calculated as a sum of the ideal-gas entropy  $S_0$  and the excess entropy  $S_{exc}$ :

$$S(T, \rho) = S_0(T) + S_{exc}(T, \rho). \quad (62)$$

The thermal EOS (19) together with the equation for internal energy (58) or enthalpy (59) determine the parametric relationships  $p$ – $\rho$ – $E$  or  $p$ – $\rho$ – $H$ , respectively, with temperature serving as a parameter.

## CHAPTER 2: OXYGEN

### 2.1. Second Virial Coefficient in the Equation of State for Oxygen

For obtaining the EOS for molecular oxygen the approach developed in Chapter 1 has been applied. The main attention in this Chapter is paid to derivation of the corresponding formulae and description of validation results related to oxygen. The thermal EOS in the form of explicit dependence of pressure  $p$  on density  $\rho$  and temperature  $T$  has been obtained for the temperature range from 280 to 3000 K and pressure up to 20 MPa.

Detailed data on thermodynamic functions of oxygen are reported in [28]. As for  $p$ – $v$ – $T$ -data provided by [28], they are available up to pressure of 100 MPa (which is much higher than considered herein) and temperature up to 1500 K (which is lower than the upper limit—3000 K—considered herein). The EOS reported in [28] is written in the form of two power series and contains 44 parameters: 42 coefficients and two critical point parameters, temperature  $T_c$  and density  $\rho_c$ . Such number of parameters is too large for CFD applications. Nevertheless, this EOS appears to be useful and feasible when applying the methodology of Chapter 1, as the latter puts stringent requirements to the accuracy of the second virial coefficient  $B$ . The structure of the EOS in [28] allows assembling the terms related to  $B$  and representing the second virial coefficient in the form of the 6th-order polynomial of inverse normalized temperature  $\tau = T/T_c$ :

$$B = \frac{1}{\rho_c} \sum_{i=0}^6 A_i \tau^{-i} \quad (63)$$

with seven coefficients:

$$A_0 = 0.5003616, \quad A_1 = -1.101003, \quad A_2 = -0.6223903,$$

$$A_3 = 0.1675656, \quad A_4 = -0.06652177,$$

$$A_5 = -0.02169624, \quad A_6 = -0.009781135$$

and critical parameters [28]:

$$T_c = 154.581 \text{ K}, \quad \rho_c = 13.6318 \text{ mol/dm}^3. \quad (64)$$

Then, the EOS takes the form:

$$p = \rho RT [1 + B\rho + b^2 \rho^2 + b^3 \rho^3], \quad (65)$$

$$b = \lambda RT_c / p_c, \quad (66)$$

where  $p_c$  is equal to [28]:

$$p_c = 5.043 \text{ MPa} \quad (67)$$

and  $\lambda$  is the dimensionless coefficient which is approximated as a function of temperature and density for alkanes (see Eq. (15)) but for oxygen the approximation

$$\lambda = \text{const} = 0.12 \quad (68)$$

proved to be sufficiently accurate.

In terms of dimensionless variables

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c.$$

Equation (65) can be rewritten as

$$\Pi = Z_c^{-1} r\tau [1 + \bar{B}r + (\bar{b}r)^2 + (\bar{b}r)^3], \quad (69)$$

where

$$\bar{B} \equiv B\rho_c = \sum_{i=0}^6 A_i \tau^{-i}, \quad (70)$$

$Z_c$  is the compressibility in the critical point,

$$Z_c \equiv p_c / (\rho_c R T_c) = 0.287843 \quad (71)$$

and

$$\bar{b} \equiv b\rho_c \equiv \lambda / Z_c = 0.41689. \quad (72)$$

Note that Eq. (69) is invariant to the choice of pressure, density, and temperature units. For the sake of convenience, two other forms of EOS (69) are given below.

If pressure, density and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho R T [1 + B\rho + (b\rho)^2 + (b\rho)^3] \quad \text{with} \quad (73)$$

$$R = 0.00831434 \text{ kJ}/(\text{mol K}).$$

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, then

$$p = \rho R_g T [1 + B_g \rho + (b_g \rho)^2 + (b_g \rho)^3], \quad (74)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad b_g = b/\mu, \quad (75)$$

and  $\mu$  is the oxygen molecular mass,

$$\mu = 31.9988 \text{ g/mol}. \quad (76)$$

To check the accuracy of Eq. (74) (as well as equivalent Eqs. (65), (69), and (73)), comparison with available data at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 1500 \text{ K}$  has been made along 11 isotherms, which is presented in Table 11. Table 11 shows that EOS (74) (and equivalent Eqs. (65), (69), and (73)) provides the accuracy of tenth or hundredth fractions of percent at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 1500 \text{ K}$ . It is important to note that discrepancy between the predictions and tabulated data of [28] is within the accuracy of tabulated data.

## 2.2. Equation of State in the Form of Virial Series for Oxygen

The EOS (65), (69), (73), or (74) with constant  $\lambda$  has the form of truncated virial series with four terms. Introducing notations:

$$\bar{C} = \bar{b}^2, \quad \bar{D} = \bar{b}^3 \quad (77)$$

one obtains from Eq. (69):

$$\Pi = r\tau / Z_c (1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (78)$$

where  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$  are the dimensionless virial coefficients. Note that at constant  $\lambda$  coefficients  $\bar{C}$  and  $\bar{D}$  are independent of temperature. As a consequence,

the calculation of thermodynamic functions is simplified considerably (see Section 2.3).

For the sake of convenience, we provide below two versions of the EOS with the explicit record of the third and fourth terms of the virial series.

If pressure, density and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho R T (1 + B\rho + C\rho^2 + D\rho^3) \quad \text{with} \quad (79)$$

$$R = 0.00831434 \text{ kJ}/(\text{mol K}),$$

where

$$C \equiv b^2, \quad D \equiv b^3, \quad (80)$$

and parameter  $b$  is given by Eq. (66).

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, one obtains:

$$p = \rho R_g T (1 + B_g \rho + C_g \rho^2 + D_g \rho^3), \quad (81)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad C_g = C/\mu^2, \quad (82)$$

$$D_g = D/\mu^3,$$

and  $\mu$  is given by Eq. (76).

## 2.3. First and Second Derivatives of Virial Coefficients for Oxygen

Because parameter  $\lambda$  entering the EOS of oxygen is independent of temperature, the derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore, one has to derive formulae for the derivatives of the second virial coefficient only. These derivatives can be derived by differentiating Eq. (63). Representing the second virial coefficient in the form

$$\bar{B} = \sum_{i=1}^6 A_i \tau^{-i}$$

one obtains the following formulae.

**First logarithmic derivative,  $\bar{B}_1$ :**

$$\bar{B}_1 \equiv \tau \frac{d\bar{B}}{d\tau} = - \sum_{i=1}^6 i A_i \tau^{-i}. \quad (83)$$

**Second logarithmic derivative,  $\bar{B}_2$ :**

$$\bar{B}_2 \equiv \tau \frac{d\bar{B}_1}{d\tau} = \sum_{i=1}^6 i^2 A_i \tau^{-i}. \quad (84)$$

## 2.4. Accuracy of Thermal Equation of State at Temperatures Exceeding 1500 K

At temperatures exceeding 1500 K, gas density is relatively low even at pressure of 20 MPa. Therefore at  $T > 1500 \text{ K}$  and  $p \leq 20 \text{ MPa}$  the accuracy of the virial EOS is mainly determined by the accuracy of the sec-

**Table 11.** Comparison of predictions given by Eq. (74) with tabulated data [28] along 11 isotherms

Isotherm $T = 300$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
52.57	3.998	4	0.05
79.52	5.994	6	0.10
106.90	7.990	8	0.13
134.52	9.986	10	0.14
203.51	14.990	15	0.07
270.27	20.03	20	0.15
Isotherm $T = 400$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
38.46	3.9993	4	0.02
57.62	5.9998	6	0.00
76.68	8.0014	8	0.02
95.61	10.006	10	0.06
142.11	15.031	15	0.21
187.06	20.09	20	0.44
Isotherm $T = 500$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
45.6	6.0008	6	0.013
60.51	8.0033	8	0.041
75.25	10.007	10	0.07
111.31	15.028	15	0.19
146.15	20.076	20	0.38
Isotherm $T = 600$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
37.86	6.6015	6	0.025
50.18	8.002	8	0.025
62.36	10.006	10	0.06
92.12	15.022	15	0.15
120.90	20.06	20	0.29
Isotherm $T = 700$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
32.41	6.0007	6	0.012
42.95	8.0013	8	0.017
53.37	10.005	10	0.05
78.83	15.017	15	0.12
103.49	20.046	20	0.23
Isotherm $T = 800$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
28.36	6.0013	6	0.022
37.58	8.00073	8	0.009
46.70	10.003	10	0.03
69.01	15.014	15	0.09
90.66	20.039	20	0.20

Table 11. (Contd.)

Isotherm $T = 900$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
25.22	6.13	6	0.022
33.43	8.0018	8	0.022
41.55	10.004	10	0.04
61.43	15.012	15	0.08
80.75	20.03	20	0.16
Isotherm $T = 1000$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
22.71	6.0007	6	0.01
30.11	8.0008	8	0.01
37.43	10.002	10	0.02
55.38	15.009	15	0.06
72.85	20.025	20	0.13
Isotherm $T = 1100$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
20.66	6.0007	6	0.001
27.40	8.001	8	0.01
34.07	10.002	10	0.02
50.44	15.008	15	0.05
66.39	20.02	20	0.10
Isotherm $T = 1300$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
79.52	5.994	6	0.10
106.90	7.990	8	0.13
134.52	9.986	10	0.14
203.51	14.990	15	0.07
270.27	20.03	20	0.15
Isotherm $T = 1500$ K			
$\rho$ , kg/m <sup>3</sup>	$p$ , MPa, calc. Eq. (74)	$p_1$ , MPa, data [28]	$ p_1 - p /p_1$ , %
15.19	6	6	0.00
20.17	8.0025	8	0.03
25.10	10.0026	10	0.03
37.24	15.0047	15	0.03
49.13	20.013	20	0.07

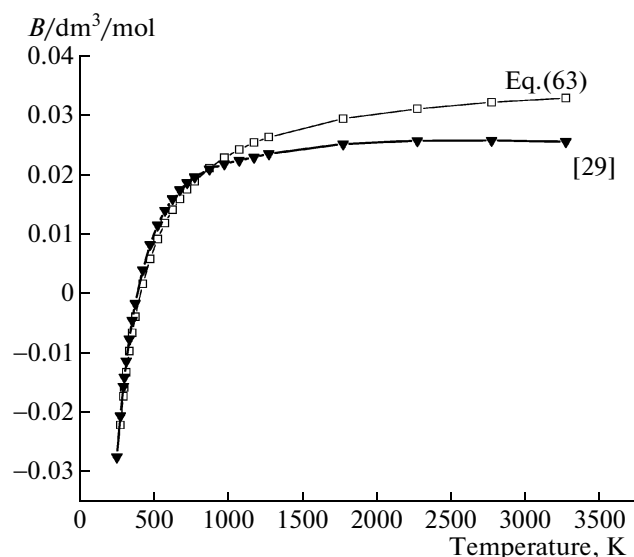


Fig. 4. Temperature dependencies of the second virial coefficient for oxygen predicted by Eq. (63) and [29].

ond virial coefficient. Equation (63) for the second virial coefficient was obtained for temperatures  $T \leq 1500$  K. However there are strong grounds to believe that application of this equation to temperatures up to 3000 K will result in insignificant errors. Curve “Eq. (63)” in Fig. 4 shows the temperature dependence of the second virial coefficient for oxygen predicted by Eq. (63). The qualitatively correct behavior of the second virial coefficient at high temperature (i.e., weak dependence on temperature, smeared maximum, and therefore nearly constant value within a wide temperature range) can be used as indication of the validity of this implication. Moreover, the approximate theoretical formula for the second virial coefficient of oxygen [29] (curve “[29]” in Fig. 4) agrees satisfactorily with the predictions provided by Eq. (63) at temperatures up to 3000 K.

Some discrepancy between the curves in Fig. 4 at high temperatures is mainly due to inconsistency of the curve provided by [29]. This curve deviates from our predictions even at  $T = 1000$ – $1500$  K, that is

within temperature interval where Eq. (74) agrees well with tables [28].

The error of Eq. (63) at temperatures  $2000 \text{ K} \leq T \leq 3000 \text{ K}$  can be as large as several percent. However, when Eq. (63) is applied for calculation of pressure, the resultant error will not exceed 1–2%. More accurate calculation of the second virial coefficient at temperatures  $\sim 3000 \text{ K}$  has no practical sense without taking into account oxygen dissociation, in particular at low pressure of 0.1 to 1 MPa.

## 2.5. Calculation of Density or Temperature Based on Other Two Variables of Thermal Equation of State

The EOS in the form of Eq. (78) (or other equivalent forms given by Eqs. (65), (69), (73), (74), (79), and (81)) provides explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively (see Section 1.5).

## 2.6. Ideal-Gas Specific Heats and Thermodynamic Functions for Oxygen

For oxygen, the ideal-gas specific heat  $C_{p0}$  is usually given in handbooks in the form of temperature polynomials. In handbook [28], the data of which were used for derivation of thermal EOS (see Chapter 1), there is a table that compares temperature dependencies of  $C_{p0}$  recommended by various researchers for the temperature range from 50 to 1500 K. Most of the recommendations are virtually the same. As reference points for constructing an approximating polynomial in [28], the data of Gurvich et al. [30] have been chosen (see second line in Table 12 below).

The polynomial for  $C_{p0}$  obtained in [28] contains 15 fitting coefficients. Such an approximation looks too complicated for CFD applications. We have obtained an approximation, which is much simpler (contains only 3 fitting parameters) and provides accuracy, which is within the accuracy of reference data. To do so, the ideal-gas specific heat was represented as a sum of two terms: ideal-gas specific heat in

Table 12. On the accuracy of approximation for  $C_{p0}$  given by Eqs. (85) and (86)

$T, \text{ K}$	300	400	500	600	700	800	900
$C_{p0}/R, [30]$	3.5344	3.6212	3.7397	3.8600	3.9673	4.0579	4.1331
$C_{p0}/R, (85), (86)$	3.5373	3.6213	3.7377	3.8572	3.9649	4.0565	4.1329
$ \delta C_{p0} /C_{p0}, \%$	0.082	0.020	0.055	0.073	0.061	0.034	0.002
$T, \text{ K}$	1000	1100	1200	1300	1400	1500	
$C_{p0}/R, [30]$	4.1951	4.2471	4.2915	4.3304	4.3655	4.3980	
$C_{p0}/R, (85), (86)$	4.1964	4.2494	4.2942	4.3325	4.3657	4.3950	
$ \delta C_{p0} /C_{p0}, \%$	0.031	0.054	0.062	0.047	0.005	0.069	

harmonic approximation for intramolecular vibrations and small correction  $\Delta$  in the form of second-order temperature polynomial. The resultant formula for the ideal-gas molar specific heat is as follows:

$$C_{p0}/R = 7/2 + x^2 \exp(x)/[\exp(x) - 1]^2 + \Delta \quad (85)$$

with

$$\Delta = 2.16 \times 10^{-3} + 1.3 \times 10^{-5} T + 1.9786 \times 10^{-8} T^2, \quad (86)$$

where

$$x = \theta/T \quad (87)$$

and  $\theta = 2272.79$  K is the characteristic vibration temperature of oxygen molecule [31]. The results of calculation of  $C_{p0}$  by using Eqs. (85) and (86) and their discrepancy from the reference data are presented in the third and fourth lines of Table 12. Clearly, the accuracy of our approximation is better than 0.1% within the entire temperature range of interest.

Integration of Eqs. (85) and (86) gives for molar enthalpy (with reference temperature  $T = 0$  K) in ideal-gas state:

$$H_0/R = 3.50216T + 6.5 \times 10^{-6} T^2 \quad (88)$$

$$+ 6.59533 \times 10^{-9} T^3 + \theta/[\exp(\theta/T) - 1].$$

Units of  $C_{p0}$  and  $H_0$  depend on the choice of units for the universal gas constant  $R$ . For example, to obtain  $C_{p0}$  and  $H_0$  in J/(mol K) and J/mol, respectively, one has to use in Eqs. (85) and (88) the value of  $R$  in J/(mol K):

$$R = 8.31434 \text{ J/(mol K)}. \quad (89)$$

To obtain  $C_{p0}$  and  $H_0$  in J/(g K) and J/g, respectively, one has to use instead of  $R$  the value of  $R/\mu$  with  $\mu = 31.9988$  g/mol in Eqs. (85) and (88), i.e.,

$$R_g \equiv R/\mu = 0.259833 \text{ J/(g K)}. \quad (90)$$

The approximation of Eq. (85) is based on the theoretically grounded relationship for oxygen specific heat at harmonic vibrations with small correction  $\Delta$  growing monotonically with temperature. This makes it possible to assume that at temperatures up to 3000 K the error of Eq. (85) for  $C_{p0}$  and, correspondingly, Eq. (88) for  $H_0$ , as well as other thermodynamic functions, will not exceed 1%. More precise calculation of  $C_{p0}$  in the temperature range between 2000 and 3000 K has no practical sense without taking into account dissociation of oxygen molecule.

The specific heats  $C_{p0}$  and  $C_{v0}$  are related to each other via the well-known thermodynamic relationships (40) or (41). The corresponding relationships between the enthalpy and the internal energy are as follows:

$$E_0 = H_0 - RT \quad (91)$$

or

$$E_0/\mu = H_0/\mu - R_g T. \quad (92)$$

The ideal-gas entropy of oxygen is given by the relationship:

$$S_0/R = \int_{T_0}^T \frac{C_{p0}}{RT} dT = 3.50216 \ln(T/T_0) \quad (93)$$

$$+ 1.3 \times 10^{-5} (T - T_0) + 9.893 \times 10^{-9} (T^2 - T_0^2)$$

$$+ S_{vib}/R + \text{const}(T_0),$$

where  $T_0$  is the reference temperature, for example, 298.15 K, and  $S_{vib}$  is the vibration component of entropy (harmonic oscillator) equal to

$$\frac{S_{vib}}{R} = \ln \frac{\exp(x_0) - 1}{\exp(x) - 1} + \frac{x}{1 - \exp(-x)} - \frac{x_0}{1 - \exp(-x_0)} \quad (94)$$

with  $x_0 = \theta/T_0$ ,  $x = \theta/T$ , and  $\theta = 2272.79$  K (see Eq. (87)). Similar to the specific heats, the units of entropy are chosen depending on the units of  $R$ .

## 2.7. Excess Thermodynamic Functions and Excess Specific Heats for Oxygen

The general formulae relating excess thermodynamic functions to the coefficients of virial series and their first and second derivatives were given in Chapter 1. Due to the fact that coefficient  $\lambda$  in the thermal EOS of oxygen is independent of temperature, the first and second derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore all excess thermodynamic functions are related only to the derivatives of the second virial coefficient.

The excess internal energy for oxygen is given by

$$E_{exc}/(RT) = -\bar{B}_1 r = -B_1 \rho, \quad (95)$$

where index 1 at virial coefficient denotes first logarithmic derivative  $\bar{B}_1 \equiv T dB/dT$ , or in the dimensionless form,  $\bar{B}_1 \equiv \tau d\bar{B}/d\tau$ . This derivative is obtained by differentiating the series of Eq. (63) and is given explicitly by Eq. (83).

Differentiation of Eq. (95) with respect to temperature gives the expression for the excess specific heat at constant volume:

$$C_{v, exc}/R = -(\bar{B}_1 + \bar{B}_2) r, \quad (96)$$

where index 2 at virial coefficient denotes second logarithmic derivative  $\bar{B}_2 \equiv \tau d\bar{B}_1/d\tau$ . This derivative is given explicitly by Eq. (84).

The excess enthalpy  $H_{exc}$  relates to the excess internal energy and the excess pressure as in Eq. (51) with

$$p_{exc}/\rho = (p - p_{id})/\rho = RT_c \tau (\bar{B} r + \bar{C} r^2 + \bar{D} r^3). \quad (97)$$

If  $H_{exc}$  and  $E_{exc}$  are taken in kJ/mol, then pressure, density, and temperature in Eq. (97) should be taken in MPa, kmol/m<sup>3</sup>, and K, respectively. In this case, the universal gas constant is taken in kJ/(mol K) and is equal to

$$R = 0.00831434 \text{ kJ/(mol K)}.$$

Differentiation of Eq. (51) with respect to temperature gives the expression for the excess specific heat at constant pressure:

$$C_{p,exc}/R = C_{v,exc}/R + \bar{B}_s r + \bar{C} r^2 + \bar{D} r^3, \quad (98)$$

where

$$\bar{B}_s \equiv d(\tau \bar{B})/d\tau \equiv \bar{B} + \bar{B}_1. \quad (99)$$

The relationships for calculating dimensionless virial coefficients  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$ , as well as derivative  $\bar{B}_1$  are provided by Eqs. (77) and (83).

The excess entropy can be calculated using the thermal  $p$ - $\rho$ - $T$  EOS using Eq. (55). Substitution of Eq. (78) in the integral of Eq. (55) gives

$$\begin{aligned} & \int_0^p [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \\ &= -R \int_0^r (\bar{B}_s + \bar{C} r + \bar{D} r^2) dr, \end{aligned} \quad (100)$$

where coefficient with index  $s$  is defined by Eqs. (99). Taking the integral in the right-hand-side of Eq. (100) allows rewriting of Eq. (55) in the final form:

$$S_{exc}/R = -\ln\left(\frac{\rho RT}{0.101325}\right) - (\bar{B}_s r + \bar{C} r^2/2 + \bar{D} r^3/3), \quad (101)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434$  kJ/(mol K).

## 2.8. Thermodynamic Functions and Specific Heats for Oxygen

Internal energy, enthalpy, specific heat at constant volume,  $C_v$ , specific heat at constant pressure,  $C_p$ , and entropy can be calculated using Eqs. (58)–(62). The thermal EOS (78) together with the equation for internal energy (58) or enthalpy (59) determine the parametric relationships  $p$ - $\rho$ - $E$  or  $p$ - $\rho$ - $H$ , respectively, with temperature serving as a parameter.

## CHAPTER 3: NITROGEN

### 3.1. Second Virial Coefficient in the Equation of State for Nitrogen

The EOS for molecular nitrogen is obtained here by using the approach developed in Chapter 1 for  $n$ -alkanes and in Chapter 2 for molecular oxygen. The thermal EOS in the form of explicit dependence of pressure  $p$  on density  $\rho$  and temperature  $T$  has been obtained for the temperature range from 280 to 3000 K and pressure up to 20 MPa.

The most complete and detailed data on the thermodynamic properties of nitrogen are available in [32] and [33]. In these references, the tabulated data on thermodynamic functions of nitrogen at pressure  $p \leq 1000$  MPa and temperature  $T \leq 1200$  K as well as at  $p \leq 10$  MPa and  $1200 \text{ K} \leq T \leq 2000$  K are presented. The

thermal EOS reported in [32] relates pressure to density and temperature in the form of a double series and contains 33 parameters. Such number of parameters is too large for CFD applications. Nevertheless, this EOS appears to be useful and feasible when applying our methodology, as the latter puts stringent requirements to the accuracy of the second virial coefficient  $B$ . The structure of the EOS in [32] allows assembling the terms related to  $B$  and representing the second virial coefficient in the form of the sum of 5 terms with 5 parameters  $A_i$ ,  $i = 1, \dots, 5$

$$B = (A_1 + A_2/T^{1/2} + A_3/T + A_4/T^2 + A_5/T^3)/R_a, \quad (102)$$

where

$$A_1 = 0.13609724 \times 10^{-2}, \quad A_2 = 0.1070285,$$

$$A_3 = -0.243926252 \times 10^1,$$

$$A_4 = 0.3412407896 \times 10^2,$$

$$A_5 = -0.4229567915 \times 10^4,$$

and

$$R_a = 0.0820562 \text{ dm}^3 \text{ atm}/(\text{mol K}) \quad (103)$$

is the universal gas constant taken in units used in [32]. We apply here this value of the universal gas constant in order to keep coefficients  $A_i$  the same as reported in [32]. Later on, this value of  $R_a$  will be used in the expressions for the derivatives of the second virial coefficient.

The thermal EOS for nitrogen takes the form:

$$p = \rho RT[1 + B\rho + b^2\rho^2 + b^3\rho^3], \quad (104)$$

where

$$b = \lambda RT_c/p_c \quad (105)$$

with  $T_c$  and  $p_c$  equal to [33]:

$$T_c = 126.193 \text{ K}, \quad p_c = 3.3978 \text{ MPa}, \quad (106)$$

and  $\lambda$  is the dimensionless coefficient which is approximated as a function of temperature and density for alkanes (see Eq. (15)) but for nitrogen the approximation

$$\lambda = \text{const} = 0.111 \quad (107)$$

proved to be sufficiently accurate (similar to oxygen, see Section 2.1). In terms of dimensionless variables

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c$$

with  $\rho_c$  equal to [33]:

$$\rho_c = 11.177 \text{ mol/dm}^3. \quad (108)$$

Equation (104) can be rewritten as

$$\Pi = Z_c^1 r \tau [1 + \bar{B} r + (\bar{b} r)^2 + (\bar{b} r)^3], \quad (109)$$

where

$$\bar{B} \equiv B\rho_c, \quad (110)$$

$$Z_c \equiv p_c/(\rho_c RT_c) = 0.28974, \quad (111)$$



and

$$\bar{b} \equiv b\rho_c \equiv \lambda/Z_c = 0.38310. \quad (112)$$

Note that Eq. (109) is invariant to the choice of pressure, density, and temperature units. For the sake of convenience, two other forms of the EOS (109) are given below.

If pressure, density and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho RT[1 + B\rho + (b\rho)^2 + (b\rho)^3] \text{ with} \quad (113)$$

$$R = 0.00831434 \text{ kJ/(mol K)}.$$

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, then

$$p = \rho R_g T[1 + B_g\rho + (b_g\rho)^2 + (b_g\rho)^3], \quad (114)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad b_g = b/\mu, \quad (115)$$

and

$$\mu = 28.0134 \text{ g/mol}. \quad (116)$$

To check the accuracy of Eq. (113) (as well as equivalent Eqs. (104), (109), and (114)), comparison with available data at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 1200 \text{ K}$  as well as at  $p \leq 10$  MPa and  $1200 \text{ K} \leq T \leq 2000 \text{ K}$  has been made along 14 isotherms which is presented in Table 13.

Table 13 shows that the EOS of Eq. (113) (and equivalent Eqs. (104), (109), and (114)) provides the accuracy of tenth or hundredth fraction of percent at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 2000 \text{ K}$ . It is important to note that discrepancy between the predictions and tabulated data of [33] is within the accuracy of tabulated data.

### 3.2. Equation of State in the Form of Virial Series for Nitrogen

The EOS (104), (109), (113), or (114) with constant  $\lambda$  have the form of truncated virial series with four terms. Introducing notations:

$$\bar{C} = \bar{b}^2, \quad \bar{D} = \bar{b}^3, \quad (117)$$

one obtains from Eq. (109):

$$\Pi = r\tau/Z_c(1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (118)$$

where  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$  are the dimensionless virial coefficients. Note that at constant  $\lambda$  coefficients  $\bar{C}$  and  $\bar{D}$  are independent of temperature. As a consequence, the calculation of thermodynamic functions is simplified considerably (see Section 3.3 below).

For the sake of convenience, we provide below two versions of the EOS with the explicit record of the third and fourth terms of virial series.

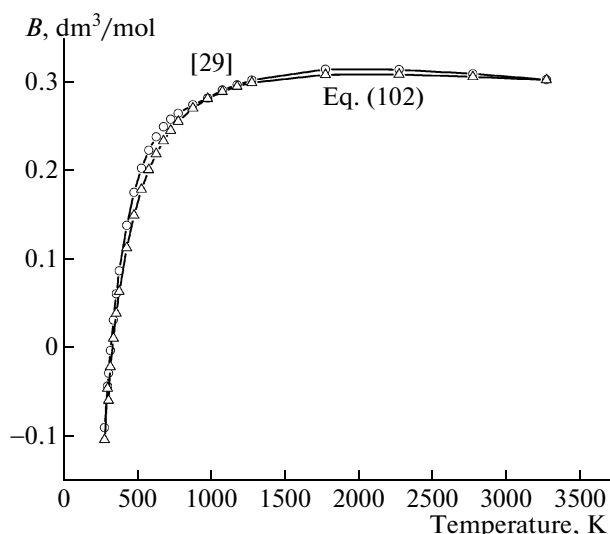


Fig. 5. Temperature dependencies of second virial coefficient for nitrogen provided by Eq. (102) and [29].

If pressure, density and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3) \text{ with} \quad (119)$$

$$R = 0.00831434 \text{ kJ/(mol K)},$$

where

$$C \equiv b^2, \quad D \equiv b^3, \quad (120)$$

and parameter  $b$  is given by Eq. (105).

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, one obtains:

$$p = \rho R_g T(1 + B_g\rho + C_g\rho^2 + D_g\rho^3), \quad (121)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad C_g = C/\mu^2, \quad (122)$$

$$D_g = D/\mu^3,$$

and  $\mu$  is given by Eq. (116).

### 3.3. First and Second Derivatives of Virial Coefficients for Nitrogen

For calculating internal energy, enthalpy, and entropy there is a need in the first logarithmic derivatives of virial coefficients. Correspondingly, for calculating specific heats there is a need in their second derivatives. Because parameter  $\lambda$  entering the EOS of nitrogen is independent of temperature, the derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore, one has to derive formulae for the derivatives of the second virial coefficient only. These derivatives can be derived by differentiating Eq. (102). The results are as follows.

**Table 13.** Comparison of predictions given by Eq. (113) with tabulated data [33] along 14 isotherms

Isotherm $T = 300$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
1.6095	3.999	4	0.038
2.4115	5.994	6	0.093
3.2057	7.990	8	0.15
3.9877	9.980	10	0.20
5.8635	14.950	15	0.33
7.5889	19.898	20	0.51
Isotherm $T = 350$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
1.3648	4.0000	4	0.001
2.0361	5.9990	6	0.017
2.6970	7.9970	8	0.037
3.3457	9.9949	10	0.051
4.9035	14.990	15	0.070
6.3554	19.982	20	0.090
Isotherm $T = 400$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
1.7683	6.0003	6	0.005
2.3386	8.0003	8	0.004
2.8976	10.000	10	0.003
4.2414	15.002	15	0.016
5.5025	20.080	20	0.040
Isotherm $T = 500$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.94635	4.0007	4	0.018
1.4070	6.0011	6	0.018
1.8590	8.0018	8	0.023
2.3020	10.002	10	0.022
3.3700	15.004	15	0.027
4.3806	20.004	20	0.022
Isotherm $T = 600$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.78816	4.0005	4	0.012
1.1718	6.0007	6	0.012
1.5485	8.0014	8	0.018
1.9181	10.002	10	0.019
2.8116	15.005	15	0.034
3.6622	20.012	20	0.060
Isotherm $T = 700$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.67594	4.0003	4	0.08
1.0054	6.0005	6	0.009
1.3292	8.0007	8	0.009
1.6474	10.001	10	0.008
2.4186	14.999	15	0.005
3.1563	19.996	20	0.021

Table 13. (Contd.)

Isotherm $T = 800$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.88099	6.0008	6	0.001
1.1654	8.0007	8	0.002
1.4452	9.9994	10	0.000
2.1252	15.000	15	0.000
2.7782	20.002	20	0.011
Isotherm $T = 900$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.52675	4.000	4	0.001
0.78432	6.000	6	0.000
1.0381	8.000	8	0.001
1.2881	10.000	10	0.001
1.8969	14.998	15	0.014
2.4835	19.994	20	0.028
Isotherm $T = 1000$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.70694	5.9996	6	0.007
0.93615	7.9992	8	0.010
1.1622	9.9986	10	0.014
1.7139	14.997	15	0.018
2.2469	19.996	20	0.020
Isotherm $T = 1200$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.59068	5.9993	6	0.012
0.78290	7.9987	8	0.016
0.97282	9.9984	10	0.022
1.3784	14.995	15	0.034
1.8893	19.993	20	0.036
Isotherm $T = 1400$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.50740	5.9991	6	0.015
0.67301	7.9985	8	0.019
0.83689	9.9976	10	0.024
Isotherm $T = 1600$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.44477	5.9991	6	0.015
0.59028	7.9983	8	0.021
0.73445	9.9975	10	0.025
Isotherm $T = 1800$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.39593	5.9991	6	0.015
0.52572	7.9984	8	0.020
0.65443	9.9974	10	0.026
Isotherm $T = 2000$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (113)	$p_1$ , MPa, data [33]	$ p_1 - p /p_1$ , %
0.35677	5.9991	6	0.015
0.47391	7.9993	8	0.021
0.59018	9.9975	10	0.025

**Table 14.** Ideal-gas specific heat  $C_{p0}$  for nitrogen [32]

$T, K$	$C_{p0}/R$	$T, K$	$C_{p0}/R$	$T, K$	$C_{p0}/R$	$T, K$	$C_{p0}/R$	$T, K$	$C_{p0}/R$	$T, K$	$C_{p0}/R$	$T, K$	$C_{p0}/R$
270	3.4995	410	3.5174	550	3.5828	690	3.6854	830	3.7982	980	3.9107	1600	4.2120
280	3.4998	420	3.5203	560	3.5892	700	3.6934	840	3.8061	990	3.9177	1650	4.2271
290	3.5001	430	3.5235	570	3.5958	710	3.7014	850	3.8139	1000	3.9246	1700	4.2413
300	3.5006	440	3.5270	580	3.6026	720	3.7095	860	3.8217	1050	3.9579	1750	4.2546
310	3.5011	450	3.5308	590	3.6095	730	3.7176	870	3.8295	1100	3.9893	1800	4.2671
320	3.5018	460	3.5349	600	3.6166	740	3.7257	880	3.8448	1150	4.0188	1850	4.2789
330	3.5027	470	3.5392	610	3.6239	750	3.7338	900	3.8524	1200	4.0465	1900	4.2899
340	3.5038	480	3.5438	620	3.6312	760	3.7419	910	3.8599	1250	4.0724	1950	4.3003
350	3.5050	490	3.5487	630	3.6387	770	3.7500	920	3.8674	1300	4.0966	2000	4.3101
360	3.5065	500	3.5538	640	3.6463	780	3.7581	930	3.8748	1350	4.1192		
370	3.5081	510	3.5591	650	3.6539	790	3.7662	940	3.8821	1400	4.1404		
380	3.5101	520	3.5647	660	3.6617	800	3.7742	950	3.8894	1450	4.1601		
390	3.5122	530	3.5705	670	3.6695	810	3.7822	960	3.8966	1500	4.1786		
400	3.5147	540	3.5765	680	3.6774	820	3.7902	970	3.9037	1550	4.1959		

**First logarithmic derivative,  $\overline{B}_1$ :**

$$\overline{B}_1 \equiv \tau \frac{d\overline{B}}{d\tau} = -\left(\frac{A_2}{2T^{1/2}} + \frac{A_3}{T} + \frac{2A_4}{T^2} + \frac{3A_5}{T^3}\right) \frac{\rho_c}{R_a}. \quad (123)$$

**Second logarithmic derivative,  $\overline{B}_2$ :**

$$\overline{B}_2 \equiv \tau \frac{d\overline{B}_1}{d\tau} = \left(\frac{A_2}{4T^{1/2}} + \frac{A_3}{T} + \frac{4A_4}{T^2} + \frac{9A_5}{T^3}\right) \frac{\rho_c}{R_a}. \quad (124)$$

Remind that the universal gas constant in Eqs. (123) and (124) is given by Eq. (103).

### 3.4. Accuracy of Thermal Equation of State at Temperatures Exceeding 2000 K

At temperatures exceeding 2000 K, gas density is relatively low even at pressure of 20 MPa. Therefore at  $T > 2000$  K and  $p \leq 20$  MPa the accuracy of the virial EOS is mainly determined by the accuracy of the second virial coefficient. Equation (102) for the second

virial coefficient was obtained for temperatures  $T \leq 1400$  K (based on [32]). However there are strong grounds to believe that application of this equation to temperatures up to 3000 K will result in insignificant errors.

Curve “Eq. (102)” in Fig. 5 shows the temperature dependence of the second virial coefficient for nitrogen predicted by Eq. (102). Qualitatively correct behavior of the second virial coefficient at high temperature (i.e., weak dependence on temperature, smeared maximum, and therefore nearly constant value within a wide temperature range) can be used as the indication of validity of this implication. Moreover, the approximate theoretical formula for the second virial coefficient of nitrogen [29] (curve “[29]” in Fig. 5) agrees satisfactorily with the predictions provided by Eq. (102) at temperatures up to 3000 K.

The error of Eq. (102) at temperatures  $2000 \text{ K} \leq T \leq 3000$  K can be as large as several percent. However, when Eq. (102) is applied for calculating pressure, the resultant error will not exceed 1–2%.

### 3.5. Calculation of Density or Temperature Based on Other Two Variables of Thermal Equation of State

The EOS (118) as well as its other equivalent forms of Eqs. (104), (109), (114), (119), and (121), provides explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively (see Section 1.5).

**Table 15.** Coefficients for the ideal-gas heat capacity equation for nitrogen [32]

Coefficient	Numerical value
$n_1$	−735.2104012
$n_2$	34.22399804
$n_3$	−0.5576482846
$n_4$	3.504042283
$n_5$	−0.1733901851E−4
$n_6$	0.1746508498E−7
$n_7$	−0.3568920335E−11
$n_8$	1.005387228

### 3.6. Ideal-Gas Specific Heats and Thermodynamic Functions for Nitrogen

In [32], a detailed table of data taken from [36] on temperature dependencies of  $C_{p0}$  for the temperature range from 50 to 1300 K has been reported. A part of this table related to temperatures above 270 K is reproduced here as Table 14.

These data were used in [32] as most reliable for the analytical approximation based on the general formula suggested by Barieau [37]. The formula contains 8 fitting parameters and is represented as a series of terms proportional to negative and positive power of temperature summed with a known term for vibrational specific heat (harmonic oscillator). The resulting formula is written as

$$C_{p0}/R = C_n(T) + n_8 x^2 \exp(x)/[\exp(x) - 1]^2 \quad (125)$$

with

$$C_n(T) = \sum_{i=1}^7 n_i T^{i-4}, \quad (126)$$

where  $x = \theta/T$ ,  $\theta = 3353.4061$  K is the characteristic vibration temperature of nitrogen molecule, and  $T$  is temperature in K. Coefficients  $n_i$  entering Eq. (126) are presented in Table 15.

The results of calculation of  $C_{p0}$  by using Eqs. (125) and (126) are presented in Fig. 6.

Integration of Eqs. (125) and (126) gives for molar enthalpy (with reference temperature  $T = T_1$ ) in the ideal-gas state:

$$H_0/R = \sum_{i=1, i \neq 3}^7 n_i [(T^{i-3} - (T_1)^{i-3})]/(i-3) + n_3 \ln(T/T_1) + n_8 \theta / [\exp(\theta/T) - 1]. \quad (127)$$

As a reference temperature for the enthalpy one can choose, for example,  $T_1 = 273.15$  K.

The units of  $C_{p0}$  and  $H_0$  depend on the choice of units for the universal gas constant  $R$ . For example, to obtain  $C_{p0}$  and  $H_0$  in J/(mol K) and J/mol, respectively, one has to use in Eqs. (125) and (127) the value of  $R$  in J/(mol K) as in Eq. (89). To obtain  $C_{p0}$  and  $H_0$  in J/(g K) and J/g, respectively, one has to use instead of  $R$  the value of  $R/\mu$  with  $\mu = 28.0134$  g/mol in Eqs. (125) and (127), i.e.,

$$R_g \equiv R/\mu = 0.29680 \text{ J/(g K)}. \quad (128)$$

The approximation of Eq. (125) is based on the theoretically grounded relationship for the specific heat of nitrogen as rigid rotator and harmonic oscillator with small correction growing monotonically with temperature. This makes it possible to assume that at temperatures up to 3000 K the error of Eq. (125) for  $C_{p0}$  and, correspondingly, Eq. (127) for  $H_0$ , as well as for other thermodynamic functions, will not exceed 1%.

Specific heats  $C_{p0}$  and  $C_{v0}$  are related to each other via the well-known thermodynamic relationships (40)

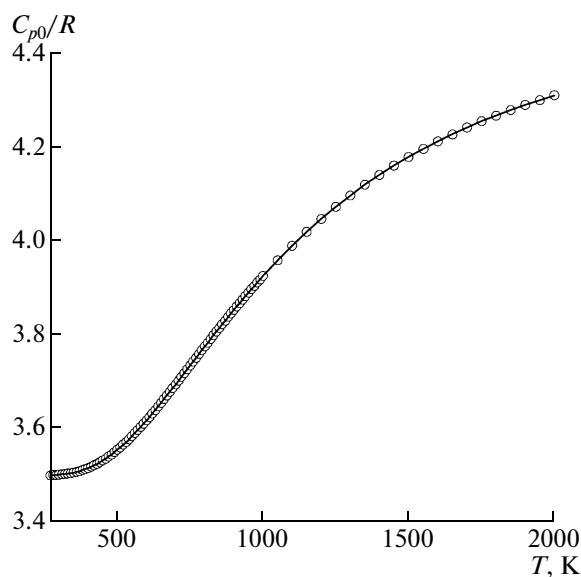


Fig. 6. Comparison of predictions provided by Eqs. (125) and (126) (curve) with reference data of Table 12.

or (41), and the corresponding relationships between the enthalpy and the internal energy are given by Eqs. (91) or (92).

The ideal-gas entropy of nitrogen is given by the relationship:

$$S_0/R = \int_{T_0}^T \frac{C_{p0}}{RT} dT = \sum_{i=1, i \neq 4} n_i [T^{i-4} - T_0^{i-4}]/(i-4) + n_4 \ln(T/T_0) + n_8 S_{vib}/R + \text{const}(T_0), \quad (129)$$

where  $T_0$  is the reference temperature, for example, 298.15 K, and  $S_{vib}$  is the vibrational component of entropy (harmonic oscillator) equal to

$$\frac{S_{vib}}{R} = \ln \frac{\exp(x_0) - 1}{\exp(x) - 1} + \frac{x}{1 - \exp(-x)} - \frac{x_0}{1 - \exp(-x_0)} \quad (130)$$

with  $x_0 = \theta/T_0$ ,  $x = \theta/T$ , and  $\theta = 3353.4061$  K. Similar to the specific heats, the units of entropy are chosen depending on the units of  $R$ .

### 3.7. Excess Thermodynamic Functions and Excess Specific Heats for Nitrogen

The general formulae relating excess thermodynamic functions to the coefficients of virial series and their first and second derivatives are given in Chapter 1. Due to the fact that coefficient  $\lambda$  in the thermal EOS of nitrogen is independent of temperature, the first and second derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore all excess thermodynamic functions are related only to the derivatives of the second virial coefficient.

**Table 16.** Second virial coefficient for steam [43, 46, 47]

$T, K$	300	400	500	600	700	800	900
$B, \text{dm}^3/\text{mol}$ [46, 47]	—	−0.33323	−0.16347	−0.09883	−0.06630	−0.04722	−0.03485
$B, \text{dm}^3/\text{mol}$ [43]	−1.11952	−0.35327	−0.17244	−0.10094	—	—	—
$T, K$	1000	1200	1400	1600	1800	2000	2400
$B, \text{dm}^3/\text{mol}$ [46, 47]	−0.02619	−0.01507	−0.00808	−0.00383	−0.00068	0.00147	0.00469
$T, K$	2600		2800		3000		
$B, \text{dm}^3/\text{mol}$ [46]	−0.02619		−0.01507		−0.00808		

The excess internal energy for oxygen is then given by

$$E_{\text{exs}}/(RT) = -\bar{B}_1 r = -B_1 \rho, \quad (131)$$

where index 1 at virial coefficient denotes the first logarithmic derivative  $\bar{B}_1 \equiv T dB/dT$ , or in the dimensionless form,  $\bar{B}_1 \equiv \tau d\bar{B}/d\tau$ . This derivative is obtained by differentiating series of Eq. (102) and is given explicitly by Eq. (123).

Differentiation of Eq. (131) with respect to temperature gives the expression for the excess specific heat at constant volume:

$$C_{v, \text{exc}}/R = -(\bar{B}_1 + \bar{B}_2)r, \quad (132)$$

where index 2 at virial coefficient denotes the second logarithmic derivative  $\bar{B}_2 \equiv \tau d\bar{B}_1/d\tau$ . This derivative is given explicitly by Eq. (124).

The excess enthalpy  $H_{\text{exc}}$  relates to the excess internal energy and the excess pressure as in Eq. (51) with

$$p_{\text{exc}}/\rho = (p - p_{\text{id}})/\rho = RT_c \tau (\bar{B}r + \bar{C}r^2 + \bar{D}r^3). \quad (133)$$

If  $H_{\text{exc}}$  and  $E_{\text{exc}}$  are taken in kJ/mol, then pressure, density, and temperature in Eq. (133) should be taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively. In this case, the universal gas constant is taken in kJ/(mol K) and equal to

$$R = 0.00831434 \text{ kJ}/(\text{mol K}).$$

Differentiation of Eq. (51) with respect to temperature gives the expression for the excess specific heat at constant pressure:

$$C_{p, \text{exc}}/R = C_{v, \text{exc}}/R + \bar{B}_s r + \bar{C}r^2 + \bar{D}r^3, \quad (134)$$

where

$$\bar{B}_s \equiv d(\tau \bar{B})/d\tau \equiv \bar{B} + \bar{B}_1. \quad (135)$$

The relationships for calculating dimensionless virial coefficients  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$ , as well as derivative  $\bar{B}_1$  are provided by Eqs. (117) and (123).

The excess entropy can be calculated using the thermal  $p$ – $\rho$ – $T$  EOS and Eq. (55). Substitution of Eq. (118) in the integral of Eq. (55) gives

$$\begin{aligned} & \int_0^\rho [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \\ &= -R \int_0^r (\bar{B}_s + \bar{C}r + \bar{D}r^2) dr, \end{aligned} \quad (136)$$

where the coefficient with index  $s$  is defined by Eqs. (135). Taking the integral in the right-hand-side of Eq. (136) allows rewriting of Eq. (55) in the final form:

$$\begin{aligned} & S_{\text{exc}}/R \\ &= -\ln\left(\frac{\rho RT}{0.101325}\right) - (\bar{B}_s r + \bar{C}r^2/2 + \bar{D}r^3/3), \end{aligned} \quad (137)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434 \text{ kJ}/(\text{mol K})$ .

### 3.8. Thermodynamic Functions and Specific Heats for Nitrogen

Internal energy, enthalpy, specific heat at constant volume,  $C_v$ , specific heat at constant pressure,  $C_p$ , and entropy can be calculated using Eqs. (58)–(62). The thermal EOS of Eq. (118) together with the equation for internal energy (58) or enthalpy (59) determine the parametric relationships  $p$ – $\rho$ – $E$  or  $p$ – $\rho$ – $H$ , respectively, with temperature serving as a parameter.

## CHAPTER 4: STEAM

### 4.1. Second Virial Coefficient in the Equation of State for Steam

For obtaining the EOS for steam the approach developed in Chapter 1 has been applied. The main attention in this Chapter is paid to derivation of the corresponding formulae and description of validation results related to steam. The thermal EOS in the form of the explicit dependence of pressure  $p$  on density  $\rho$  and temperature  $T$  has been obtained for the tempera-

ture range from 280 to 3000 K and pressure up to 20 MPa.

Detailed data on thermodynamic functions of steam within wide ranges of pressure and temperature are reported in [5, 38, 39]. In terms of pressure, such data exist up to pressure of 200 MPa, which is far beyond our interest. However in terms of temperature, such data are limited by the values of 800–1000°C only. Experimental  $p$ – $v$ – $T$  data at temperatures  $400^\circ\text{C} \leq T \leq 1000^\circ\text{C}$  and pressure up to 1000 atm have been reported in [40]. These data do not pretend to high accuracy however they were obtained by direct measurements of specific volume as a function of pressure and temperature. International system of equations used in [5] and other equations of this type contain tens and even hundreds of parameters. Such number of parameters is too large for CFD applications. Multiparameter thermal EOS for steam were also obtained in [41]. In 70s and 80s of last century, equations for Helmholtz potential have been published elsewhere [42–45]. These equations were derived by means of processing various thermal and calorific experimental data. These equations also contain many tens of parameters. A rather wide bibliography on thermodynamic data of steam has been reported in [45].

To construct the thermal EOS for steam with relatively small number of parameters feasible for CFD applications, we have used available data on the second virial coefficient within the temperature range  $400\text{ K} \leq T \leq 3000\text{ K}$  [46, 47] and  $300\text{ K} \leq T \leq 600\text{ K}$  [43]. These data are reproduced here in Table 16.

To obtain the first analytical approximation for the second virial coefficient we used the expression (see Eq. (7))

$$B = RT_c f / p_c, \quad (138)$$

where  $T_c$  and  $p_c$  are equal to [44]

$$T_c = 647.14\text{ K}, \quad p_c = 22.064\text{ MPa}, \quad (139)$$

and

$$f = f_0 + \omega f_1. \quad (140)$$

Note that in order to obtain  $B$  in  $\text{dm}^3/\text{mol}$  based on Eqs. (138) and (139), one has to use the following value of the universal gas constant:  $R = 0.00831434\text{ kJ}/(\text{mol K})$ .

At any value of Pitzer factor, function  $f$  is given by

$$f = A_0 + A_1/\tau + A_2/\tau^2 + A_3/\tau^3 + A_8/\tau^8, \quad (141)$$

$$\tau \equiv T/T_c.$$

Coefficients  $A_0, A_1, \dots$  entering Eq. (141) depend on  $\omega$  and can be obtained based on data [6] for the coefficients of functions  $f_0$  and  $f_1$  (see Eqs. (8) and (9)). However such calculations made with the Pitzer factor for steam ( $\omega = 0.344$  [47]) resulted in  $B$  values deviating considerably from the data of Table 16. To overcome this difficulty, we refrained from such a method to calculate coefficients  $A_0, A_1, \dots$  implying that the

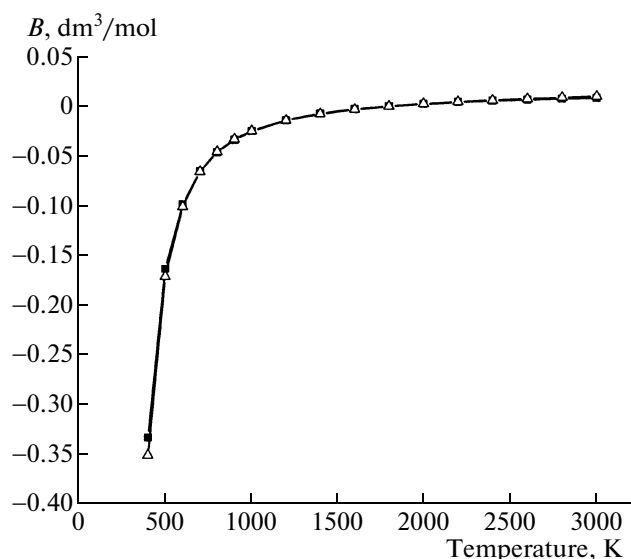


Fig. 7. Second virial coefficient for steam. Squares—[46], triangles—Eqs. (138), (141), and (142).

general dependency of function  $f$  on temperature remains as given by Eq. (141). With this in mind, we have obtained all 5 coefficients entering Eq. (141) by using nonlinear regression analysis and data of Table 16 (the data in the third line of Table 16 at temperature below and equal to 600 K and the data in the second line of Table 16 at higher temperatures). As a result, the following values of coefficients in Eq. (141) have been obtained:

$$A_0 = 0.104, \quad A_1 = -0.357, \quad A_2 = 0.296, \quad (142)$$

$$A_3 = -0.377, \quad A_8 = -0.003.$$

The results of calculations of the second virial coefficient for steam using Eqs. (138), (141), and (142) as well as the tabulated data of [46] are presented in Fig. 7.

The EOS of steam then takes the form:

$$p = \rho RT [1 + B\rho + b^2\rho^2 + b^3\rho^3], \quad (143)$$

$$b = \lambda RT_c / p_c, \quad (144)$$

where, as before,  $\lambda$  is the dimensionless coefficient which can be approximated as a function of temperature and density based on available  $p$ – $v$ – $T$  data. For steam, the approximation

$$\lambda = \text{const} = 0.16 \quad (145)$$

proved to be sufficiently accurate. In terms of dimensionless variables

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c$$

with

$$\rho_c = 17.889\text{ mol}/\text{dm}^3. \quad (146)$$

Equation (143) can be rewritten as

$$\Pi = Z_c^1 r \tau [1 + \bar{B}r + (\bar{b}r)^2 + (\bar{b}r)^3] \quad (147)$$

with

$$Z_c \equiv p_c / (\rho_c R T_c) = 0.22923, \quad (148)$$

$$\bar{B} \equiv B \rho_c, \quad (149)$$

and

$$\bar{b} \equiv b \rho_c \equiv \lambda / Z_c = 0.69799. \quad (150)$$

Equation (147) is invariant to the choice of pressure, density, and temperature units.

For the sake of convenience, the two other forms of EOS (143) are given below. If pressure, density and temperature are taken in MPa, mol/dm<sup>3</sup>, and K, respectively, one has

$$p = \rho R T [1 + B \rho + (b \rho)^2 + (b \rho)^3] \text{ with} \quad (151)$$

$$R = 0.00831434 \text{ kJ/(mol K)}.$$

If pressure, density, and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, then

$$p = \rho R_g T [1 + B_g \rho + (b_g \rho)^2 + (b_g \rho)^3], \quad (152)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad b_g = b/\mu, \quad (153)$$

and

$$\mu = 18.01534 \text{ g/mol}. \quad (154)$$

#### 4.2. Local Correction of Second Virial Coefficient for Steam

When checking the accuracy of the thermal EOS by comparing predicted pressure values with tabulated data it was found that some correction is required in the vicinity of the saturation curve (in the temperature range  $t \approx (170 \pm 100)^\circ\text{C}$ ) to ensure the same accuracy level throughout the ranges of pressure and temperature considered herein. In this temperature range, the density of steam is relatively small. Therefore the arising error in the thermal EOS is mainly due to uncertainties in the value of the second virial coefficient. To diminish this uncertainty, we have introduced a small correction  $\Delta$  in the form of modified Gauss function to the equation for the second virial coefficient:

$$\Delta = \alpha \exp(-0.6\Psi) + \gamma \exp(-\Psi) \text{ dm}^3/\text{mol} \quad (155)$$

$$\Psi = k(T - T_0)^2,$$

where

$$\alpha = 0.005951 \text{ dm}^3/\text{mol},$$

$$\gamma = 9.6808 \times 10^{-3} \text{ dm}^3/\text{mol},$$

$$T_0 = 439.87 \text{ K},$$

$$k = 1.6899 \times 10^{-4} \text{ K}^{-2}.$$

In the dimensionless form, the correction of Eq. (155) is rewritten as

$$\bar{\Delta} \equiv \rho_c \Delta = \bar{\alpha} \exp(-0.6\Psi) + \bar{\gamma} \exp(-\Psi),$$

$$\bar{\alpha} = 0.1065, \quad (156)$$

$$\bar{\gamma} = 0.1732.$$

The corrected relationship for the second virial coefficient is

$$B = R T_c f / p_c - \Delta, \quad (157)$$

or, in terms of dimensionless variables,

$$\bar{B} = f / Z_c - \bar{\Delta}. \quad (158)$$

To check the accuracy of Eq. (143) (as well as equivalent Eqs. (147), (151), and (152)) with the corrected relationship for the second virial coefficient (i.e., Eq. (157) or (158)), comparison with available data at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 1073 \text{ K}$  has been made along 9 isotherms which is presented in Table 17.

At temperatures below  $260^\circ\text{C}$  steam is very rarefied even at the saturation curve and, correspondingly, the error of the EOS is low. Tables 18 and 19 compare the tabulated and predicted data for overheated steam in the vicinity of the saturation curve at low temperatures (Table 18) and at the saturation curve up to temperatures very close to the critical temperature (Table 19).

Tables 17 to 19 indicate that the EOS (152) (and equivalent Eqs. (143), (147), and (151)) provides the accuracy of tenth or hundredth fractions of percent at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 1073 \text{ K}$  except for the saturation curve at high pressures and relatively low temperatures close to the critical temperature of water ( $647.14 \text{ K}$ ), where the approximation error attains 1%. It is important to note that discrepancy between the predictions and tabulated data of [38] is within the accuracy of the tabulated data.

#### 4.3. Equation of State in the Form of Virial Series for Steam

In approximation  $\lambda = \text{const}$ , Eq. (147) (and other its equivalents) has the form of the truncated virial series with four terms. Introducing the notations

$$\bar{C} = \bar{b}^2, \quad \bar{D} = \bar{b}^3, \quad (159)$$

one obtains from Eq. (147):

$$\Pi = r\tau / Z_c (1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (160)$$

where  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$  are the dimensionless virial coefficients. Note that at constant  $\lambda$ , coefficients  $\bar{C}$  and  $\bar{D}$  are independent of temperature. As a consequence, the calculation of thermodynamic functions is simplified considerably. Equation (160) with the coefficients given by Eqs. (159) are equivalent to Eq. (147).

For the sake of convenience, we provide below two versions of the EOS with the explicit record of the third and fourth terms of the virial series.



**Table 17.** Comparison of predictions given by Eqs. (152), (157) with tabulated data [38] along 9 isotherms

Isotherm $t = 260^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	5.174			4.454					
$p_1, \text{MPa, data [38]}$	4			4.5					
$p, \text{MPa, calc. Eqs. (152), (157)}$	4.017			4.529					
$ p_1 - p /p_1, \%$	0.42			0.66					
Isotherm $t = 280^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	5.547		4.224		3.317				
$p_1, \text{MPa, data [38]}$	4		5		6				
$p, \text{MPa, calc. Eqs. (152), (157)}$	4.010		5.026		6.054				
$ p_1 - p /p_1, \%$	0.25		0.53		0.91				
Isotherm $t = 300^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	5.885	4.532	3.616	2.976	2.425				
$p_1, \text{MPa, data [38]}$	4	5	6	7	8				
$p, \text{MPa, calc. Eqs. (152), (157)}$	4.0066	5.017	6.033	7.0052	8.090				
$ p_1 - p /p_1, \%$	0.17	0.34	0.55	0.07	1.1				
Isotherm $t = 320^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	6.200	4.811	3.876	3.199	2.682	2.268	1.924		
$p_1, \text{MPa, data [38]}$	4	5	6	7	8	9	10		
$p, \text{MPa, calc. Eqs. (152), (157)}$	4.0047	5.011	6.021	7.0358	8.055	9.080	10.107		
$ p_1 - p /p_1, \%$	0.12	0.22	0.35	0.51	0.68	0.89	1.06		
Isotherm $t = 350^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	6.645	5.194	4.223	3.524	2.995	2.242	1.721	1.323	1.148
$p_1, \text{MPa, data [38]}$	4	5	6	7	8	10	12	14	15
$p, \text{MPa, calc. Eqs. (152), (157)}$	4.0024	5.006	6.011	7.019	8.030	10.056	12.083	14.081	15.042
$ p_1 - p /p_1, \%$	0.006	0.13	0.18	0.27	0.37	0.56	0.69	0.58	0.28
Isotherm $t = 400^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	7.339	4.738	3.431	2.641	2.108	1.722	1.427	1.191	0.9952
$p_1, \text{MPa, data [38]}$	4	6	8	10	12	14	16	18	20
$p, \text{MPa, calc. Eqs. (152), (157)}$	4.0005	6.0047	8.011	10.023	12.043	14.067	16.093	18.125	20.156
$ p_1 - p /p_1, \%$	0.012	0.066	0.014	0.23	0.36	0.48	0.58	0.69	0.78
Isotherm $t = 500^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	8.638	5.662	4.172	3.277	2.679	2.251	1.929	1.678	1.477
$p_1, \text{MPa, data [38]}$	4	6	8	10	12	14	16	18	20
$p, \text{MPa, calc. Eqs. (152), (157)}$	3.998	5.996	7.996	9.998	12.005	14.018	16.041	18.076	20.12
$ p_1 - p /p_1, \%$	0.05	0.06	0.04	0.02	0.04	0.13	0.26	0.42	0.60
Isotherm $t = 600^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	9.879	6.521	4.841	3.833	3.161	2.681	2.321	2.041	1.816
$p_1, \text{MPa, data [38]}$	4	6	8	10	12	14	16	18	20
$p, \text{MPa, calc. Eqs. (152), (157)}$	3.996	5.992	7.988	9.985	11.984	13.985	15.991	18.003	20.034
$ p_1 - p /p_1, \%$	0.09	0.13	0.14	0.15	0.13	0.11	0.06	0.02	0.17
Isotherm $t = 800^{\circ}\text{C}$									
$v \times 100, \text{dm}^3/\text{g}$	7.339	8.161	6.098	4.860	4.035	3.446	3.004	2.660	2.386
$p_1, \text{MPa, data [38]}$	4	6	8	10	12	14	16	18	20
$p, \text{MPa, calc. Eqs. (152), (157)}$	3.993	5.986	7.977	9.967	11.956	13.945	15.938	17.935	19.927
$ p_1 - p /p_1, \%$	0.18	0.23	0.29	0.33	0.37	0.39	0.39	0.36	0.36

**Table 18.** Comparison of predictions given by Eqs. (152) and (157) with tabulated data [38] in the vicinity of the saturation curve at low temperatures

$t, ^\circ\text{C}$	100	150	200	230
$v \times 100, \text{dm}^3/\text{g}$	212.7	63.4	13.24	10.53
$p_1, \text{MPa, data [38]}$	0.08	0.3	1.5	2
$p, \text{MPa, calc. Eqs. (152), (157)}$	0.08000	0.29982	1.50026	2.00026
$ p_1 - p /p_1, \%$	0.00	0.06	0.02	0.01

**Table 19.** Comparison of predicted and tabulated [38] pressure along the saturation curve for water

$p_1$ , MPa, data [38]	1		2		3		4		5			
$t$ , °C	179.88		212.37		233.84		250.33		263.92			
$v \times 100$ , dm <sup>3</sup> /g	19.43		9.953		6.662		4.974		3.941			
$p$ , MPa, calc. Eqs. (152), (157)	1.000		2.003		3.010		4.024		5.042			
$ p_1 - p /p_1$ , %	0.00		0.13		0.35		0.60		0.84			
$p_1$ , MPa, data [38]	6		7		8		9		10			
$t$ , °C	275.56		285.80		294.98		303.31		310.96			
$v \times 100$ , dm <sup>3</sup> /g	3.241		2.734		2.349		2.046		1.800			
$p$ , MPa, calc. Eqs. (152), (157)	6.063		7.085		8.106		9.12		10.13			
$ p_1 - p /p_1$ , %	1.06		1.2		1.3		1.3		1.3			
$p_1$ , MPa, data [38]	11		12		13		14		15		16	
$t$ , °C	318.04		324.64		330.81		336.63		342.12		347.32	
$v \times 100$ , dm <sup>3</sup> /g	1.597		1.425		1.277		1.149		1.035		0.933	
$p$ , MPa, calc. Eqs. (152), (157)	11.127		12.114		13.083		14.029		14.948		15.84	
$ p_1 - p /p_1$ , %	1.16		0.95		0.64		0.19		0.35		1.0	

If pressure, density and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3) \text{ with } R = 0.00831434 \text{ kJ/(mol K)}, \quad (161)$$

where

$$C \equiv b^2, \quad D \equiv b^3, \quad (162)$$

and parameter  $b$  is given by Eqs. (144) and (145).

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, one obtains:

$$p = \rho R_g T(1 + B_g \rho + C_g \rho^2 + D_g \rho^3), \quad (163)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad C_g = C/\mu^2, \quad D_g = D/\mu^3, \quad (164)$$

and  $\mu$  is given by Eq. (154).

It should be emphasized that Eq. (160) is no more than one of possible approximations for the thermal EOS in the form of virial series with a given finite number of terms. All coefficients in this equation, except for first two (1 and  $B$ ), are not the true virial coefficients.

#### 4.4. First and Second Derivatives of Virial Coefficients for Steam

The first and second logarithmic derivatives of virial coefficients needed for calculating thermodynamic functions can be obtained by differentiating Eq. (158). The results of differentiation can be represented in explicit dependencies on temperature as follows.

Representing the dimensionless second virial coefficient in the form

$$\bar{B} = \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i} - \bar{\Delta}, \quad (165)$$

where  $\bar{\Delta}$  is the small correction defined by Eq. (156) and  $\bar{A}_i = A_i/Z_c$ ,  $i = 0, 1, 2, 3, 8$ , one obtains:

**First logarithmic derivative,  $\bar{B}_1$ :**

$$\bar{B}_1 \equiv \tau \frac{d\bar{B}}{d\tau} = - \left( \sum_{i=1,2,3,8} i \bar{A}_i \tau^{-i} \right) - \tau \frac{d\bar{\Delta}}{d\tau}, \quad (166)$$

$$\tau \frac{d\bar{\Delta}}{d\tau} \equiv \bar{\Delta}_1 = -2kT(T - T_0) \times [0.6\alpha \exp(-0.6\Psi) + \gamma \exp(-\Psi)]. \quad (167)$$

**Table 20.** Comparison of pressure predictions given by Eq. (138) ( $p_2$ ) and second virial coefficient of Table 16 [46] ( $p_1$ ) for isobar 20 MPa

Isobar $p = 20$ MPa					
$T$ , K	1400	1800	2200	2600	3000
$v \times 100$ , dm <sup>3</sup> /g	3.200	4.1620	5.1045	6.0420	6.9712
$p_1$ , MPa	20.01	20.004	20.0005	19.994	20.00016
$p_2$ , MPa	19.994	19.995	20.0086	20.010	20.024
$ p_1 - p /p_1$ , %	0.082	0.046	0.040	0.082	0.12

**Second logarithmic derivative,  $\bar{B}_2$ :**

$$\bar{B}_2 \equiv \tau \frac{d\bar{B}_1}{d\tau} = \sum_{i=1,2,3,8} i^2 \bar{A}_i \tau^{-i} - \tau \frac{d\bar{\Delta}_1}{d\tau}, \quad (168)$$

$$\tau \frac{d\bar{\Delta}_1}{d\tau} = -2kT(2T - T_0)[0.6\alpha \exp(-0.6\Psi) + \gamma \exp(-\Psi)] + 4k^2 T^2 (T - T_0)[0.36\alpha \exp(-0.6\Psi) + \gamma \exp(-\Psi)]. \quad (169)$$

#### 4.5. Accuracy of Thermal Equation of State at Temperatures 1070 K < $T$ < 3000 K

At temperatures exceeding 1070 K, gas density is relatively low even at pressure of 20 MPa. Therefore at  $T > 1070$  K and  $p \leq 20$  MPa the accuracy of the virial EOS is mainly determined by the accuracy of the second virial coefficient. Equation (138) for the second virial coefficient was obtained for temperatures  $T \leq 3000$  K. At temperatures  $1400 \text{ K} \leq T \leq 3000 \text{ K}$ , the approximation of Eq. (138) gives the results, which differ by 10–20% from tabulated data [46]. However due to low density this does not result in significant errors in the predicted pressure. The most indicative in this respect is the isobar  $p = 20$  MPa. At this isobar, the error in pressure predicted by Eq. (138) is maximal. Table 20 compares the pressures obtained by using the second virial coefficient from Table 16 [46] ( $p_1$ ) and by using Eq. (138) ( $p_2$ ).

Weak dependence of pressure on variation of the second virial coefficient at high temperatures and pressures allows one to anticipate that the error of the EOS (143) at temperatures  $1070 \text{ K} \leq T \leq 3000 \text{ K}$  and pressures up to 20 MPa is of the same order as in Table 20, i.e., not worse than 0.1–0.3%. More accurate calculation of the second virial coefficient at temperatures  $\sim 3000$  K has no practical sense without taking into account steam dissociation, in particular at low pressures from 0.1 to 1 MPa.

#### 4.6. Calculation of Density or Temperature Based on Other Two Variables of Thermal Equation of State

The EOS (143) and all its equivalent forms provide explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need

of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively (see Section 1.5).

#### 4.7. Ideal-Gas Specific Heats and Thermodynamic Functions for Steam

There exist a number of publications on isobaric specific heat  $C_{p0}$  and enthalpy  $H_0$  of steam. A detailed bibliography on thermodynamic functions of steam in the ideal-gas state is reported elsewhere [45]. At relatively low temperatures (approximately up to 1600 K), various approximations for  $C_{p0}$  agree usually with each other within the accuracy of tenth fractions of percent. For example, the polynomial approximation

$$C_{p0} = 7.701 + 4.495 \times 10^{-4} T + 2.521 \times 10^{-4} T^2 - 8.59 \times 10^{-10} T^3 \text{ cal/(mol K)}$$

provided in [19] corresponds with the tabulated data of [46] within this accuracy.

With temperature increase, the contributions of inharmonic molecular vibrations and excitations of electronic levels become significant. Therefore discrepancy between theoretical approximations increases attaining the value of about 1% at temperatures close to 3000 K. In view of it, we recommend a formula for  $C_{p0}$  represented as a sum of two terms—ideal-gas specific heat in harmonic approximation for molecular vibrations and small correction  $\delta C_{p0}$ . Such approximation for  $C_{p0}$  is preferable as it allows simple analytical integration. Explicitly, it is given below:

$$C_{p0}/R = 4 + \sum_{i=1}^3 x_i^2 \exp(x_i) / [\exp(x_i) - 1]^2 + \delta C_{p0}/R \quad (170)$$

with

$$\delta C_{p0}/R = 0.021083 - 2.87826 \times 10^{-5} T + 5.14474 \times 10^{-8} T^2 \quad (171)$$

or

$$\delta C_{p0} = 0.17529 - 2.39308 \times 10^{-4} T + 4.27751 \times 10^{-7} T^2, \quad (172)$$

**Table 21.** Accuracy of approximation for  $C_{p0}$  given by Eqs. (170) and (171)

$T, \text{ K}$	300	400	500	600	700	800	1000
$C_{p0}, \text{ J/(mol K) [46]}$	33.618	34.146	35.071	36.289	37.606	38.942	41.544
$C_{p0}, \text{ J/(mol K) (170), (171)}$	33.632	34.299	35.281	36.401	37.589	38.828	41.389
$ \delta C_{p0} /C_{p0}, \%$	0.041	0.45	0.6	0.34	0.045	0.29	0.38
$T, \text{ K}$	1200	1500	2000	2200	2500	3000	
$C_{p0}, \text{ J/(mol K) [46]}$	43.969	47.215	51.600	53.030	54.873	57.274	
$C_{p0}, \text{ J/(mol K) (170), (171)}$	43.900	47.270	51.616	52.995	54.798	57.350	
$ \delta C_{p0} /C_{p0}, \%$	0.16	0.12	0.032	0.066	0.14	0.13	

where  $x_i = \theta_i/T$ ;  $\theta_1 = 5260.73 \text{ K}$ ,  $\theta_2 = 2294.37 \text{ K}$ , and  $\theta_3 = 5403.36 \text{ K}$  are the characteristic vibration temperatures of water molecule [31], and  $T$  is temperature in K. To obtain correction  $\delta C_{p0}$ , we have used quadratic approximation of the difference between the tabulated values of  $C_{p0}$  in handbook [46] and term

$$\left\{ 3 + \sum_{i=1}^3 x_i^2 \exp(x_i) / [\exp(x_i) - 1]^2 \right\} R$$

within temperature interval  $300 \text{ K} \leq T \leq 3000 \text{ K}$ . Before deriving Eq. (171), the fourth significant digits in tabulated data of [46] were smoothed at temperature values of  $T = 800, 900, 1000$ , and  $1300 \text{ K}$ .

The results of calculation of  $C_{p0}$  by using Eqs. (170) and (171) and their discrepancy from the tabulated data of [46] are presented in Table 21. It follows from Table 21 that the error of approximations (170), (171) does not exceed 0.2–0.3%. This error is comparable with the error of tabulated data [46].

Integration of Eqs. (170) and (171) results in the expression for the molar enthalpy (with reference temperature  $T = 0 \text{ K}$ ) in the ideal-gas state:

$$H_0/(RT) = 4.021083 - 1.413913 \times 10^{-5} T + 1.714913 \times 10^{-8} T^2 + \sum_{i=1}^3 \frac{x_i}{\exp(x_i) - 1}. \quad (173)$$

The units of  $C_{p0}$  and  $H_0$  depend on the choice of units for the universal gas constant  $R$ . For example, to obtain  $C_{p0}$  and  $H_0$  in J/(mol K) and J/mol, respectively, one has to use in Eqs. (170) and (173) the value of  $R = 8.31434 \text{ J/(mol K)}$ . To obtain  $C_{p0}$  and  $H_0$  in J/(g K) and J/g, respectively, one has to use the value of  $R/\mu$  with  $\mu = 18.01534 \text{ g/mol}$  instead of  $R$  in Eqs. (170) and (172), i.e.,

$$R_g \equiv R/\mu = 0.46151805 \text{ J/(g K)}. \quad (174)$$

The approximation of Eq. (170) is based on the theoretically grounded relationship for the specific heat of water for harmonic vibrations with small correction  $\delta C_{p0}$  growing monotonically with temperature. As was mentioned above, at  $T = 3000 \text{ K}$  the error of Eq. (170) for  $C_{p0}$  due to possible error of tabulated data and, correspondingly, Eq. (173) for  $H_0$ , as well as for

other thermodynamic functions is around 1%. More precise calculation of  $C_{p0}$  in the temperature range between 2500 and 3000 K has no practical sense without taking into account water molecule dissociation.

Specific heats  $C_{p0}$  and  $C_{v0}$  are related to each other via the well-known thermodynamic relationships (40) or (41), and the corresponding relationships between the enthalpy and the internal energy are given by Eqs. (91) or (92).

The ideal-gas entropy of steam is given by the relationship:

$$S_0/R = \int_{T_0}^T \frac{C_{p0}}{RT} dT = 4.021083 \ln(T/T_0) - 2.87826 \times 10^{-5} (T - T_0) + 2.57237 \times 10^{-8} (T^2 - T_0^2) + S_{vib}/R + \text{Const}(T_0), \quad (175)$$

where  $T_0$  is the reference temperature, for example,  $298.15 \text{ K}$ , and  $S_{vib}$  is the vibrational entropy (harmonic oscillator) equal to

$$S_{vib}/R = \sum_{i=1}^3 \left[ \ln \frac{\exp(x_{i0}) - 1}{\exp(x_i) - 1} + \frac{x_i}{1 - \exp(-x_i)} - \frac{x_{i0}}{1 - \exp(-x_{i0})} \right]. \quad (176)$$

Similar to the specific heats, the units of entropy are chosen depending on the units of  $R$ .

#### 4.8. Excess Thermodynamic Functions and Excess Specific Heats for Steam

The general formulae relating excess thermodynamic functions to the coefficients of virial series and their first and second derivatives are given in Chapter 1.

The excess internal energy for steam is given by

$$E_{exc}/(RT) = -\bar{B}_1 r = -B_1 \rho, \quad (177)$$

where index 1 denotes the first logarithmic derivative  $B_1 \equiv T dB/dT$ . This derivative is obtained by differentiating Eqs. (158) with respect to temperature. The

**Table 22.** Second virial coefficient for carbon monoxide [30]

<i>T</i> , K	293.15	298.15	400	500	600	700	800
<i>B</i> , 10 <sup>−3</sup> dm <sup>3</sup> /mol [30]	−10.04	−8.88	7.64	16.57	22.14	25.85	28.49
<i>T</i> , K	900	1000	1200	1400	1600	1800	2000
<i>B</i> , 10 <sup>−3</sup> dm <sup>3</sup> /mol [30]	30.39	31.80	33.48	34.76	35.65	36.19	36.36
<i>T</i> , K	2200	2400	2600	2800	3000		
<i>B</i> , 10 <sup>−3</sup> dm <sup>3</sup> /mol [30]	36.58	36.70	36.74	36.67	36.50		

explicit expression for the derivative is given by Eqs. (166), (167).

Differentiation of Eq. (177) with respect to temperature gives the expression for the excess specific heat at constant volume:

$$C_{v,exc}/R = -\overline{B}_{2t}r = -(\overline{B}_1 + \overline{B}_2)r, \quad (178)$$

where index *2t* denotes the second derivative  $\overline{B}_{2t} \equiv d(\tau \overline{B}_1)/d\tau = \overline{B}_1 + \overline{B}_2$ . Derivatives  $\overline{B}_1$  and  $\overline{B}_2$  are given explicitly by Eqs. (166), (167), (168), and (169).

The excess enthalpy  $H_{exc}$  relates to the excess internal energy and the excess pressure as in Eq. (51) with

$$p_{exc}/\rho = (p - p_{id})/\rho = RT_c\tau(\overline{B}r + \overline{C}r^2 + \overline{D}r^3). \quad (179)$$

Differentiation of Eq. (51) with respect to temperature gives the expression for the excess specific heat at constant pressure:

$$C_{p,exc}/R = C_{v,exc}/R + \overline{B}_s r + \overline{C}r^2 + \overline{D}r^3, \quad (180)$$

where

$$\overline{B}_s \equiv d(\tau \overline{B})/d\tau \equiv \overline{B} + \overline{B}_1. \quad (181)$$

The relationships for calculating dimensionless virial coefficients  $\overline{B}$ ,  $\overline{C}$ , and  $\overline{D}$  as well as derivative  $\overline{B}_1$  are given explicitly by Eqs. (158), (159), (166), and (167).

The excess entropy can be calculated using  $p$ – $\rho$ – $T$  equation of state and Eq. (55).

Substitution of Eq. (160) in integral of Eq. (55) gives

$$\begin{aligned} & \int_0^p [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \\ &= -R \int_0^r (\overline{B}_s + \overline{C}r + \overline{D}r^2) dr, \end{aligned} \quad (182)$$

where the coefficients with index *s* are defined by Eqs. (181). Taking the integral in the right-hand-side of Eq. (182) allows rewriting of Eq. (55) in the final form:

$$\begin{aligned} & S_{exc}/R \\ &= -\ln\left(\frac{\rho RT}{0.101325}\right) - (\overline{B}_s r + \overline{C}r^2/2 + \overline{D}r^3/3), \end{aligned} \quad (183)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434$  kJ/(mol K).

#### 4.9. Thermodynamic Functions and Specific Heats for Steam

Internal energy, enthalpy, specific heat at constant volume,  $C_v$ , specific heat at constant pressure,  $C_p$ , and entropy can be calculated using Eqs. (58)–(62). The thermal EOS (143) together with the equation for internal energy (58) or enthalpy (59) determines the parametric relationships  $p$ – $\rho$ – $E$  or  $p$ – $\rho$ – $H$ , respectively, with temperature serving as a parameter.

### CHAPTER 5: CARBON MONOXIDE

#### 5.1. Second Virial Coefficient in the Equation of State for Carbon Monoxide

For obtaining the EOS for carbon monoxide the approach developed in Chapter 1 has been applied. The thermal EOS in the form of explicit dependence of pressure  $p$  on density  $\rho$  and temperature  $T$  has been obtained for temperature range from 280 to 3000 K and pressure up to 20 MPa.

Detailed data on the second virial coefficient of carbon monoxide within wide range of temperature are reported in [30] and reproduced here in Table 22.

To obtain the analytical approximation for the second virial coefficient we used the expression (see Eqs. (7)–(9)):

$$B = a_0 + a_1/\tau + a_2/\tau^2 + a_3/\tau^3 + a_8/\tau^8 \text{ dm}^3/\text{mol}, \quad (184)$$

where  $\tau \equiv T/T_c$ , and the critical temperature  $T_c$  of carbon monoxide is [48]:

$$T_c = 134.45 \text{ K}. \quad (185)$$

The values of coefficients  $a_0, a_1, \dots, a_8$  in Eq. (184) were determined by nonlinear regression analysis based on  $B$  values of Table 22 (dimension dm<sup>3</sup>/mol):

$$\begin{aligned} a_0 &= 3.6445 \times 10^{-2}, & a_1 &= 3.5253 \times 10^{-2}, \\ a_2 &= -0.62523, & a_3 &= 0.813693, & a_8 &= -5.089. \end{aligned} \quad (186)$$

#### 5.2. Thermal Equation of State for Carbon Monoxide

Detailed data on thermodynamic functions of carbon monoxide as well as relevant bibliography are

reported elsewhere [48]. As for  $p$ – $v$ – $T$ -data reported in [48], they are available up to a pressure of 100 MPa (which is much higher than pressures considered herein) and temperatures up to 1000 K (which is lower than the upper limit—3000 K—considered herein). The EOS reported in [48] is written in the form of the multistage functional dependency of pressure on density and temperature containing many tens of parameters. Such EOS are too complex for CFD applications.

Our objective was to construct a simpler EOS possessing accuracy, which is sufficient for CFD applications at temperatures and pressures ranging from 280 to 3000 K and up to 20 MPa, respectively. To implement this objective, we applied the methodology of Chapter 1 and Eqs. (184), (186) as a first approximation for the second virial coefficient  $B$ . Later on, when determining the parameters of the thermal EOS based on  $p$ – $v$ – $T$  tables of [48], the coefficients given by Eq. (186) were corrected (see Eqs. (192) and (193) below).

The EOS is taken in the form:

$$p = \rho RT[1 + B\rho + b^2\rho^2 + b^3\rho^3], \quad (187)$$

$$b = \lambda RT_c/p_c \quad (188)$$

with  $p_c$  equal to [48]:

$$p_c = 3.506 \text{ MPa} \quad (189)$$

and with the approximation for  $\lambda$

$$\lambda = \text{const} = 0.115. \quad (190)$$

To obtain better accuracy at low temperatures, we had to correct expression (184) for the second virial coefficient by multiplying the right-hand-side of Eq. (184) by a factor of 0.93. This allowed us to attain better agreement of predictions based on Eq. (187) with tabulated data [30].

Thus, coefficients  $a_0, a_1, \dots, a_8$  given by Eqs. (186) were replaced by coefficients  $A_0, A_1, \dots, A_8$  (dimension  $\text{dm}^3/\text{mol}$ ):

$$\begin{aligned} A_0 &= 3.3894 \times 10^{-2}, & A_1 &= 3.27853 \times 10^{-2}, \\ A_2 &= -0.581464, & A_3 &= 0.756734, \\ A_8 &= -4.7328. \end{aligned} \quad (191)$$

The corrected expression for the second virial coefficient is then given by

$$\begin{aligned} B &= A_0 + A_1/\tau + A_2/\tau^2 + A_3/\tau^3 \\ &+ A_8/\tau^8 \text{ dm}^3/\text{mol}. \end{aligned} \quad (192)$$

In terms of dimensionless variables,

$$\bar{B} = \bar{A}_0 + \bar{A}_1/\tau + \bar{A}_2/\tau^2 + \bar{A}_3/\tau^3 + \bar{A}_8/\tau^8, \quad (193)$$

where  $\bar{A}_i = A_i/p_c$ ,  $i = 0, 1, 2, 3$ , and 8.

In the final form, the thermal EOS for carbon monoxide is represented by Eq. (187) with the coefficients determined by Eqs. (188), (190), (191), and (192).

It is worth to present the other (equivalent) forms of Eq. (187). If pressure, density and temperature are taken in MPa,  $\text{kg}/\text{m}^3$ , and K, respectively, then

$$p = \rho R_g T[1 + B_g \rho + (b_g \rho)^2 + (b_g \rho)^3], \quad (194)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad b_g = b/\mu, \quad (195)$$

and

$$\mu = 28.011 \text{ g/mol}.$$

In terms of dimensionless variables

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c \quad (196)$$

with [48]

$$\rho_c = 11.10 \text{ mol/dm}^3 \quad (197)$$

(the values of other critical parameters are given above by Eqs. (185) and (189)), Eq. (187) can be transformed to

$$\Pi = Z_c^{-1} r \tau [1 + \bar{B}r + (\bar{b}r)^2 + (\bar{b}r)^3], \quad (198)$$

where

$$\bar{B} \equiv B/p_c, \quad (199)$$

$$Z_c \equiv p_c/(\rho_c RT_c) = 0.282553, \quad (200)$$

$$\bar{b} \equiv b/p_c \equiv \lambda/Z_c = 0.407003. \quad (201)$$

To check the accuracy of Eq. (187) (as well as equivalent Eqs. (194) and (198)), comparison with available data [48] at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 1000 \text{ K}$  has been made along 10 isotherms, which is presented in Table 23.

Table 23 shows that EOS (187) (and equivalent Eqs. (194) and (198)) provides the accuracy better than 0.2% at  $p \leq 20$  MPa and  $400 \text{ K} \leq T \leq 1000 \text{ K}$ . At temperatures less than 400 K, the accuracy is somewhat worse and attains 1.6% at  $T = 280 \text{ K}$  and pressure of 20 MPa. Keeping in mind that compression in piston engines results in temperatures significantly higher than 280 K, the accuracy of Eq. (187) should be treated as very good. It is important to note that discrepancy between predictions and tabulated data of [48] is within the accuracy of tabulated data in [48].

### 5.3. Equation of State in the Form of Virial Series for Carbon Monoxide

The EOS in the form of Eq. (187) (as well as Eq. (194) or Eq. (198)) with constant  $\lambda$  has the form of truncated virial series with four terms. Introducing notations:

$$\bar{C} = \bar{b}^2, \quad \bar{D} = \bar{b}^3 \quad (202)$$

(where  $\bar{b} = 0.407003$ , see Eq. (201)) one obtains from Eq. (198):

$$\Pi = r\tau/Z_c(1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (203)$$

where  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$  are the dimensionless virial coefficients. Note that at constant  $\lambda$  coefficients  $\bar{C}$  and  $\bar{D}$  are independent of temperature. As a consequence,

**Table 23.** Comparison of predictions given by Eq. (187) with tabulated data [48] along 10 isotherms

Isotherm $T = 280$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
1.74279	3.976	4	0.61
2.61978	5.936	6	1.06
3.49509	7.888	8	1.39
4.36502	9.842	10	1.58
5.22381	11.802	12	1.65
6.06411	13.770	14	1.64
6.87803	15.743	16	1.61
7.65862	17.715	18	1.58
8.40098	19.680	20	1.60
Isotherm $T = 300$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
1.6149	3.992	4	0.19
2.41981	5.974	6	0.44
3.21878	7.952	8	0.59
4.00928	9.936	10	0.64
4.78791	11.930	12	0.58
5.55036	13.936	14	0.46
6.29186	15.953	16	0.29
7.00785	17.977	18	0.13
7.69473	20.002	20	0.01
Isotherm $T = 350$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
1.36891	4.001	4	0.03
2.04203	5.994	6	0.09
2.70506	7.985	8	0.18
3.35702	9.979	10	0.21
3.99687	11.980	12	0.17
4.62332	13.989	14	0.08
5.23489	16.009	16	0.06
5.83004	18.039	18	0.22
6.40734	20.076	20	0.38
Isotherm $T = 400$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
1.19093	4.002	4	0.06
1.77288	5.998	6	0.04
2.34427	7.990	8	0.12
2.90469	9.983	10	0.17
3.45382	11.979	12	0.17
3.99131	13.981	14	0.14
4.51671	15.989	16	0.07
5.02953	18.005	18	0.03
5.52927	20.029	20	0.14

**Table 23.** (Contd.)

Isotherm $T = 500$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
0.94818	4.004	4	0.09
1.40962	6.002	6	0.04
1.86196	7.999	8	0.01
2.30518	9.994	10	0.06
2.73932	11.990	12	0.08
3.16448	13.988	14	0.09
3.58073	15.989	16	0.07
3.98813	17.994	18	0.03
4.38673	20.004	20	0.02
Isotherm $T = 600$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
0.78916	4.004	4	0.099
1.17315	6.005	6	0.077
1.54979	8.004	8	0.045
1.91912	10.002	10	0.016
2.28124	11.999	12	0.005
2.63631	13.998	14	0.014
2.98446	15.998	16	0.011
3.32584	18.001	18	0.005
3.66057	20.006	20	0.032
Isotherm $T = 700$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
0.67642	4.003	4	0.086
1.00590	6.005	6	0.075
1.32943	8.004	8	0.056
1.64706	10.003	10	0.034
1.95891	12.002	12	0.017
2.26509	14.001	14	0.006
2.56574	16.000	16	0.002
2.86100	18.001	18	0.008
3.15099	20.004	20	0.021
Isotherm $T = 800$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
0.59215	4.003	4	0.063
0.88099	6.003	6	0.056
1.16494	8.003	8	0.039
1.44407	10.002	10	0.021
1.71846	12.000	12	0.004
1.98822	13.999	14	0.010
2.25346	15.997	16	0.018
2.51429	17.996	18	0.021
2.77084	19.997	20	0.017



Table 23. (Contd.)

Isotherm $T = 900$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
0.52671	4.002	4	0.041
0.78399	6.002	6	0.031
1.03720	8.001	8	0.013
1.28640	9.999	10	0.007
1.53166	11.997	12	0.026
1.77307	13.994	14	0.042
2.01072	15.991	16	0.055
2.24470	17.988	18	0.064
2.47510	19.986	20	0.068
Isotherm $T = 1000$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (187)	$p_1$ , MPa, data [48]	$ p_1 - p /p_1$ , %
0.47437	4.001	4	0.018
0.70641	6.000	6	0.005
0.93500	7.999	8	0.016
1.16022	9.996	10	0.037
1.38210	11.993	12	0.060
1.60074	13.989	14	0.079
1.81619	15.984	16	0.097
2.02854	17.980	18	0.111
2.23786	19.976	20	0.122

the calculation of thermodynamic functions is simplified considerably (see Section 5.4 below).

For the sake of convenience, we provide below two alternative versions of the EOS with explicit record of third and fourth terms of virial series.

If pressure, density and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3) \text{ with} \quad (204)$$

$$R = 0.00831434 \text{ kJ}(\text{mol K}),$$

where

$$C \equiv b^2, \quad D \equiv b^3, \quad (205)$$

and parameter  $b$  is given by Eqs. (188) and (190).

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, one obtains:

$$p = \rho R_g T(1 + B_g \rho + C_g \rho^2 + D_g \rho^3), \quad (206)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad C_g = C/\mu^2, \quad (207)$$

$$D_g = D/\mu^3,$$

and  $\mu = 28.011$  g/mol.

#### 5.4. First and Second Derivatives of Virial Coefficients for Carbon Monoxide

Because parameter  $\lambda$  entering the EOS of carbon monoxide is independent of temperature, the derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore, one has to derive formulae for the derivatives of the second virial coefficient only. These derivatives can be derived by differentiating Eq. (193). Introducing notation

$$\bar{B} = \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i} \quad (208)$$

one obtains:

**First logarithmic derivative,  $\bar{B}_1$ :**

$$\bar{B}_1 \equiv \tau \frac{d\bar{B}}{d\tau} = - \sum_{i=1,2,3,8} i \bar{A}_i \tau^{-i}. \quad (209)$$

**Second logarithmic derivative,  $\bar{B}_2$ :**

$$\bar{B}_2 \equiv \tau \frac{d\bar{B}_1}{d\tau} = \sum_{i=1,2,3,8} i^2 \bar{A}_i \tau^{-i}. \quad (210)$$

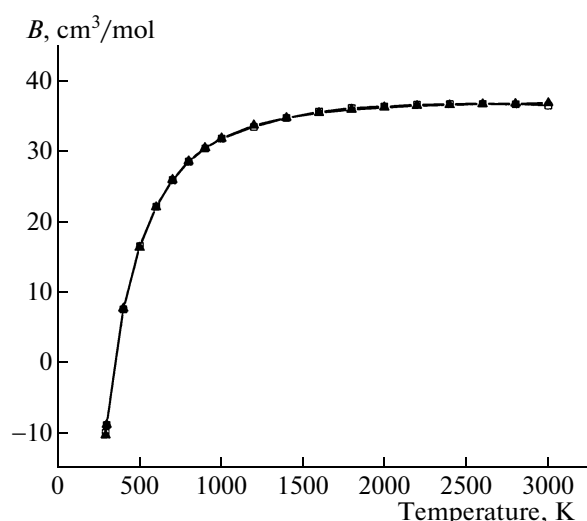


Fig. 8. Temperature dependencies of the second virial coefficient for carbon monoxide. Squares—[30], triangles—Eq. (184).

#### 5.5. Accuracy of Thermal Equation of State at Temperatures Exceeding 1000 K

At temperatures exceeding 1000 K, gas density is relatively low even at pressure of 20 MPa. Therefore at  $T > 1000$  K and  $p \leq 20$  MPa the accuracy of the virial EOS is mainly determined by the accuracy of the second virial coefficient. Equations (184) and (186) for the second virial coefficient were obtained for temperatures  $T \leq 3000$  K. The corrected formula (192) was derived based on  $p$ – $v$ – $T$  tables [48], limited by temperature 1000 K. Therefore its application to higher temperatures should be treated as extrapolation. However, good agreement of predicted and tabulated pressures at temperatures below 1000 K and qualitatively correct behavior of the second virial coefficient at high temperature (i.e., weak dependence on temperature, smeared maximum, and therefore nearly constant value within a wide temperature range, see Fig. 8) allow one to believe that Eq. (192) provides better performance than Eq. (184), at least at  $T < 1500$  K. For estimating the error associated with the use of the EOS

at higher temperatures, we have compared predicted pressures with  $B$  provided by Eqs. (184) and (192). Such a comparison is presented in Table 24 for isobar  $p = 20$  MPa and in Table 25 for isotherm  $T = 3000$  K.

Based on Tables 22 and 23 one can anticipate that the error associated with the use of Eq. (187) (or equivalent Eqs. (194) and (198)) at temperatures  $1500 \text{ K} \leq T \leq 3000 \text{ K}$  and pressures up to 20 MPa can be of several tenth fractions of percent with a maximum value of about 1%.

#### 5.6. Calculation of Density or Temperature Based on Other Two Variables of Thermal Equation of State

The EOS (187) provides explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively (see Section 1.5).

#### 5.7. Ideal-Gas Specific Heats and Thermodynamic Functions for Carbon Monoxide

For carbon monoxide, detailed tabulated data on the ideal-gas specific heat  $C_{p0}$  within temperature range  $60 \text{ K} \leq T \leq 2700 \text{ K}$  are presented elsewhere [2, 39]. The analytical approximation of tabulated data [39] for temperature range  $60 \text{ K} \leq T \leq 1400 \text{ K}$  is presented in [48]. It is given by the formula

$$C_{p0}/R = 3.5 + \exp(-\varepsilon/x) \sum_{i=1}^5 N_i x^{2-i}, \quad (211)$$

where  $x = T/100$ , and

$$\begin{aligned} \varepsilon &= 17.80, \\ N_1 &= 0.059485855, \\ N_2 &= -1.70764979, \\ N_3 &= 67.483204, \\ N_4 &= -315.657869, \\ N_5 &= 432.946687. \end{aligned}$$

Table 24. Comparison of pressures predicted by using Eqs. (184) and (192) for the second virial coefficient along isobar  $p = 20$  MPa

Isobar $p = 20$ MPa				
$T$ , K	$\rho$ , mol/dm <sup>3</sup>	$p_1$ , MPa, calc. Eq. (192)	$p$ , MPa, calc. Eq. (184)	$ p_1 - p /p_1$ , %
1500	1.52280	20	20.071	0.36
1600	1.43165	20	20.068	0.34
1800	1.278794	20	20.061	0.31
2000	1.155577	20	20.056	0.28
2500	0.931491	20	20.046	0.23
3000	0.78031	20	20.039	0.20

There are several drawbacks of Eq. (211). First, it does not cover the entire temperature interval  $280\text{ K} \leq T \leq 3000\text{ K}$  considered herein. Second, it cannot be integrated analytically to obtain simple correlations for enthalpy, internal energy, and entropy. We have obtained the other approximation, which overcomes these drawbacks. To do so, the ideal-gas specific heat was represented as a sum of two terms: ideal-gas specific heat in harmonic approximation for molecular vibrations and small correction  $\Delta$  in the form of the first-order temperature polynomial. The resultant formula for the ideal-gas molar specific heat is as follows:

$$C_{p0}/R = 7/2 + x^2 \exp(x)/[\exp(x) - 1]^2 + \Delta \quad (212)$$

with

$$\Delta = -0.00162 + 2.08 \times 10^{-5} T, \quad (213)$$

$$280\text{ K} \leq T \leq 3000\text{ K},$$

where  $x = \theta/T$ ,  $\theta = 3122.23\text{ K}$  is the characteristic vibration temperature of carbon monoxide [31], and  $T$  is temperature in K. The results of calculation of  $C_{p0}$  by using Eqs. (212) and (213) and their discrepancy from reference data are presented in Table 26.

As follows from Table 26, the approximation error of  $C_{p0}$  obtained from Eqs. (212) and (213) is less than 0.1% within the entire temperature range of interest. This error is of the same order as the error of tabulated data in [48].

Integration of Eqs. (212) and (213) gives the expression for the molar enthalpy (with reference temperature  $T = 0\text{ K}$ ) in the ideal-gas state:

$$H_0/(RT) = 3.4984 + 1.04 \times 10^{-5} T + \frac{x}{\exp(x) - 1}. \quad (214)$$

The units of  $C_{p0}$  and  $H_0$  depend on the choice of units for the universal gas constant  $R$ . For example, to obtain  $C_{p0}$  and  $H_0$  in J/(mol K) and J/mol, respectively, one has to use in Eqs. (212) and (214) the value  $R = 8.31434\text{ J/(mol K)}$ . To obtain  $C_{p0}$  and  $H_0$  in J/(g K) and J/g, respectively, one has to use the value of  $R/\mu$  with  $\mu = 28.011\text{ g/mol}$  instead of  $R$  in Eqs. (212) and (214), i.e.,

$$R_g \equiv R/\mu = 0.29682\text{ J/(g K)}. \quad (215)$$

The approximation of Eq. (212) is based on the theoretically grounded relationship for the specific heat of carbon monoxide taking into account harmonic molecular vibrations with small correction  $\Delta$  growing monotonically with temperature. This makes it possible to assume that at temperatures up to 3000 K the error of Eqs. (212), (213) for  $C_{p0}$  and, correspondingly, Eq. (214) for  $H_0$ , as well as for other thermodynamic functions, will be the same order as in Table 26, i.e. less than 1%.

The specific heats  $C_{p0}$  and  $C_{v0}$  are related via the well-known thermodynamic relationships (40) or (41). The corresponding relationships between the enthalpy and the internal energy are given by Eq. (91) or (92).

**Table 25.** Comparison of pressures predicted by using Eqs. (184) and (192) for the second virial coefficient along isotherm  $T = 3000\text{ K}$

Isotherm $T = 3000\text{ K}$			
$\rho$ , mol/dm <sup>3</sup>	$p_1$ , MPa, calc. Eq. (192)	$p$ , MPa, calc. Eq. (184)	$ p_1 - p /p_1$ , %
0.23858	6.0000	6.0037	0.061
0.31724	8.0000	8.0065	0.081
0.39543	10.0000	10.010	0.10
0.51202	13.0000	13.0168	0.13
0.62760	16.0000	16.0254	0.16

The ideal-gas entropy of carbon monoxide is given by the relationship:

$$S_0/R = \int_{T_0}^T \frac{C_{p0}}{RT} dT = 3.4984 \ln(T/T_0) \quad (216)$$

$$+ 2.08 \times 10^{-5} (T - T_0) + S_{vib}/R + \text{const}(T_0),$$

where  $T_0$  is the reference temperature, for example, 298.15 K, and  $S_{vib}$  is the vibration component of entropy (harmonic oscillator) equal to

$$\frac{S_{vib}}{R} = \ln \frac{\exp(x_0) - 1}{\exp(x) - 1} + \frac{x}{1 - \exp(-x)} - \frac{x_0}{1 - \exp(-x_0)}. \quad (217)$$

Similar to specific heats, the units of entropy are chosen depending on the units of  $R$ .

### 5.8. Excess Thermodynamic Functions and Excess Specific Heats for Carbon Monoxide

Due to the fact that coefficient  $\lambda$  in the thermal EOS of carbon monoxide is independent of temperature, the first and second derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore all excess thermodynamic functions are related only to the derivatives of second virial coefficient.

The excess internal energy for carbon monoxide is given by

$$E_{exc}/(RT) = -\bar{B}_1 r = -B_1 \rho. \quad (218)$$

The derivative  $\bar{B}_1$  is given explicitly by Eq. (209).

Differentiation of Eq. (218) with respect to temperature gives the expression for the excess specific heat at constant volume:

$$C_{v,exc}/R = -(\bar{B}_1 + \bar{B}_2) r. \quad (219)$$

The derivative  $\bar{B}_2$  is given explicitly by Eq. (210).

**Table 26.** Accuracy of approximation for  $C_{p0}$  given by Eqs. (212) and (213)

$T, K$	$C_p,$ J/(mol K) Eq. (212)	$C_{p0},$ J/(mol K) [2]	$\delta C_{p0}/C_{p0},$ %
280	29.150	29.126	-0.083
290	29.157	29.134	-0.080
300	29.166	29.142	-0.081
400	29.362	29.343	-0.068
500	29.805	29.792	-0.045
600	30.442	30.440	-0.007
700	31.165	31.171	0.020
800	31.888	31.903	0.049
900	32.562	32.576	0.042
1000	33.167	33.183	0.048
1100	33.699	33.707	0.023
1200	34.162	34.174	0.034
1300	34.563	34.572	0.026
1400	34.910	34.913	0.008
1500	35.212	35.220	0.023
1600	35.475	35.478	0.009
1700	35.705	35.703	-0.006
1800	35.907	35.910	0.008
1900	36.087	36.085	-0.004
2000	36.246	36.243	-0.007
2100	36.388	36.385	-0.009
2200	36.516	36.509	-0.019
2300	36.632	36.626	-0.014
2400	36.736	36.734	-0.006
2500	36.832	36.826	-0.017
2600	36.920	36.917	-0.007
2700	37.000	37.000	0.00002

The excess enthalpy  $H_{exc}$  relates to the excess internal energy and the excess pressure as in Eq. (51) with

$$p_{exc}/\rho = (p - p_{id})/\rho = RT_c \tau (\bar{B}r + \bar{C}r^2 + \bar{D}r^3) \quad (220)$$

and  $p_{id}$  is the ideal-gas pressure. Coefficient  $\bar{B}$  is given by Eq. (193) or (208). Coefficients  $\bar{C}$  and  $\bar{D}$  are given by Eqs. (202).

If  $H_{exc}$  and  $E_{exc}$  are taken in kJ/mol, then pressure, density, and temperature in Eq. (220) should be taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively. In this case, the universal gas constant is taken in kJ/(mol K) and is equal to

$$R = 0.00831434 \text{ kJ/(mol K)}.$$

Differentiation of Eq. (51) with respect to temperature gives the expression for the excess specific heat at constant pressure:

$$C_{p,exc}/R = C_{v,exc}/R + \bar{B}_s r + \bar{C}r^2 + \bar{D}r^3, \quad (221)$$

where

$$\bar{B}_s \equiv d(\tau \bar{B})/d\tau \equiv \bar{B} + \bar{B}_1. \quad (222)$$

Coefficient  $\bar{B}$  is given by Eq. (193) or (208), whereas coefficient  $\bar{B}_1$  is given by Eq. (209).

The excess entropy can be calculated using  $p$ - $\rho$ - $T$  EOS and Eq. (55). Substituting the EOS of Eq. (203) in the integral of Eq. (55) gives

$$\begin{aligned} & \int_0^p [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \\ &= -R \int_0^r (\bar{B}_s + \bar{C}r + \bar{D}r^2) dr. \end{aligned} \quad (223)$$

Taking the integral in the right-hand-side of Eq. (223) allows rewriting of Eq. (55) in the final form:

$$\begin{aligned} & S_{exc}/R \\ &= -\ln\left(\frac{\rho RT}{0.101325}\right) - (\bar{B}_s r + \bar{C}r^2/2 + \bar{D}r^3/3), \end{aligned} \quad (224)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434 \text{ kJ/(mol K)}$ .

### 5.9. Thermodynamic Functions and Specific Heats for Carbon Monoxide

Internal energy, enthalpy, specific heat at constant volume,  $C_v$ , specific heat at constant pressure,  $C_p$ , and entropy can be calculated using Eqs. (58)–(62). The thermal EOS (187) together with the equation for internal energy (58) or enthalpy (59) determines the parametric relationships  $p$ - $\rho$ - $E$  or  $p$ - $\rho$ - $H$ , respectively, with temperature serving as a parameter.

## CHAPTER 6: CARBON DIOXIDE

### 6.1. Second Virial Coefficient in the Equation of State for Carbon Dioxide

For obtaining the EOS for carbon dioxide the approach developed in Chapter 1 has been applied. The thermal EOS in the form of explicit dependence of pressure  $p$  on density  $\rho$  and temperature  $T$  has been obtained for temperature range from 280 to 3000 K and pressure up to 20 MPa.

Detailed data on the second virial coefficient of carbon dioxide within wide range of temperature are reported in [49, 50]. However, the values of the second virial coefficient in these references do not correspond well to each other (Fig. 9).

Reference [49] was published later than handbook [50]. Tabulated data in [49], including data on the second virial coefficient, were obtained based on critical analysis and selection of previous results. Tables of  $p$ – $v$ – $T$  properties available in [49], which were obtained by using data on the second virial coefficient presented in [49], agree with thermodynamic tables [2, 39] within the accuracy of 0.3–0.5% with respect to pressure. The discrepancy of the results is systematic: at the same values of density and temperature, the pressure in tables [2] is somewhat larger. Our estimates and control calculations of pressure (i.e.,  $p$ – $v$ – $T$  dependencies) indicate that the data on the second virial coefficient presented in [50] lead to larger deviations from tables [2, 39] as compared with the data of [49]. The latter are reproduced here in Table 27.

In [49], the approximation for the second virial coefficient has been suggested which is too complex to be used in the current analysis. To obtain a simpler analytical approximation for the second virial coefficient we used the same approach as for carbon monoxide (see Eq. (184)):

$$B = a_0 + a_1/\tau + a_2/\tau^2 + a_3/\tau^3 + a_8/\tau^8 \text{ cm}^3/\text{g}, \quad (225)$$

where  $\tau \equiv T/T_c$ , and [2, 49]:

$$T_c = 304.19 \text{ K}. \quad (226)$$

The values of coefficients  $a_0, a_1, \dots, a_8$  in Eq. (225) were determined by nonlinear regression analysis based on  $B$  values of [49] in Table 27 (dimension  $\text{cm}^3/\text{g}$ ):

$$\begin{aligned} a_0 &= 0.836, & a_1 &= -0.686, & a_2 &= -3.135, \\ a_3 &= 0.29, & a_8 &= -0.007. \end{aligned} \quad (227)$$

Coefficients  $a_0, a_1, \dots, a_8$  in Eq. (227) were purposefully taken in  $\text{cm}^3/\text{g}$  to directly compare the predicted and tabulated values of  $B$  in Table 27. Clearly, Eqs. (225) and (227) approximate the tabulated data (second line in Table 27) with the accuracy of the order of tenth fractions of percent (excluding the vicinity of the Boyle point, where the absolute values of the second virial coefficient are low and it does not contribute to the thermal EOS). Note that the approximation error obtained is much less than the actual error of tabulated data on the second virial coefficient.

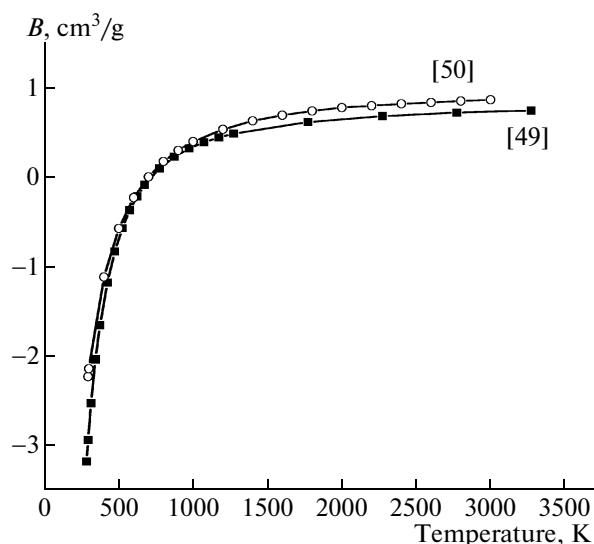


Fig. 9. Available temperature dependencies (reported in [49] and [50]) of the second virial coefficient for carbon dioxide.

## 6.2. Thermal Equation of State for Carbon Dioxide

Detailed data on thermodynamic functions of carbon dioxide are reported elsewhere [2, 39, 49]. Extensive bibliography on the issue till 1965 is reported in [49]; the  $p$ – $v$ – $T$  data in [49] are limited by pressure of 60 MPa, which covers the range of our interest. As for temperature,  $p$ – $v$ – $T$  data of [49] are limited by 1273 K (which is lower than the upper limit—3000 K—considered herein). Tables of [2, 39] cover the temperature range up to 1500 K, however, they are limited by the maximum pressure of 10 MPa [2], which is insufficient for our purposes. It was mentioned in Section 6.1 that the  $p$ – $v$ – $T$  data on pressure (at specified density and temperature) correspond to each other within tenth fractions of percent in average.

Our objective was to construct a simple EOS, which would provide accuracy sufficient for CFD applications at temperatures and pressures ranging from 280 to 3000 K and up to 20 MPa, respectively. To implement this objective, we applied the methodology

Table 27. Second virial coefficient for carbon dioxide [49] and its approximation by Eq. (225)

$t, ^\circ\text{C}$	10	20	40	70	100	150	200
$B, \text{cm}^3/\text{g}$ [49]	–3.17509	–2.93374	–2.52264	–2.03489	–1.65370	–1.17513	–0.827273
$B, \text{cm}^3/\text{g}$ Eq. (225)	–3.17204	–2.93680	–2.52828	–2.03631	–1.65083	–1.17000	–0.823950
$t, ^\circ\text{C}$	250	300	350	400	500	600	700
$B, \text{cm}^3/\text{g}$ [49]	–0.566145	–0.365318	–0.207773	–0.082032	0.103578	0.231853	0.324603
$B, \text{cm}^3/\text{g}$ Eq. (225)	–0.565886	–0.367835	–0.212197	–0.087431	0.098468	0.228775	0.324110
$t, ^\circ\text{C}$	800	900	1000	1500	2000	2500	3000
$B, \text{cm}^3/\text{g}$ [49]	0.394299	0.448424	0.491661	0.621620	0.687224	0.726251	0.751328
$B, \text{cm}^3/\text{g}$ Eq. (225)	0.396267	0.452405	0.497086	0.627514	0.688755	0.723414	0.745403

of Chapter 1 and Eq. (225) as a first approximation for the second virial coefficient  $B$ . Later on, when determining parameters of the thermal EOS based on  $p$ – $v$ – $T$  tables of [49], the coefficients given by Eq. (227) were corrected (see Eqs. (232) and (233) below).

The EOS was taken in the form:

$$p = \rho RT[1 + B\rho + b^2\rho^2 + b^3\rho^3], \quad (228)$$

$$b = \lambda RT_c/p_c \quad (229)$$

with  $p_c$  equal to [49]:

$$p_c = 72.9 \text{ atm} = 7.3870 \text{ MPa}, \quad (230)$$

and

$$\lambda = \text{const} = 0.115. \quad (231)$$

To obtain better accuracy at low temperatures, we had to correct the expression (225) for the second virial coefficient by multiplying the right-hand-side of Eq. (225) by parameter  $s$  equal to

$$s = 1.015 - 0.487928 \exp(-\sigma T), \quad \sigma = 0.00512, \quad (232)$$

where  $T$  is taken in Kelvin. This allowed us to obtain better agreement of the predictions based on Eq. (228) with tabulated data [49].

The corrected expression for the second virial coefficient is now given as

$$B = \left( a_0 + \frac{a_1}{\tau} + \frac{a_2}{\tau^2} + \frac{a_3}{\tau^3} + \frac{a_8}{\tau^8} \right) s \text{ cm}^3/\text{g}, \quad (233)$$

or

$$B = \left( A_0 + \frac{A_1}{\tau} + \frac{A_2}{\tau^2} + \frac{A_3}{\tau^3} + \frac{A_8}{\tau^8} \right) s \text{ dm}^3/\text{mol}, \quad (234)$$

where coefficients  $A_0, A_1, \dots, A_8$  are given by (dimension  $\text{dm}^3/\text{mol}$ ):

$$\begin{aligned} A_0 &= 3.6792 \times 10^{-2}, & A_1 &= -3.0191 \times 10^{-2}, \\ A_2 &= -0.13797, & A_3 &= 0.01276, \\ A_8 &= -3.081 \times 10^{-4}. \end{aligned} \quad (235)$$

In terms of dimensionless variables, Eq. (234) can be rewritten as

$$\bar{B} = \left( \bar{A}_0 + \frac{\bar{A}_1}{\tau} + \frac{\bar{A}_2}{\tau^2} + \frac{\bar{A}_3}{\tau^3} + \frac{\bar{A}_8}{\tau^8} \right) s, \quad (236)$$

where  $\bar{A}_i = A_i \rho_c$ ,  $i = 0, 1, 2, 3$ , and 8, and  $\rho_c$  is equal to [49]:

$$\rho_c = 10.6337 \text{ mol/dm}^3. \quad (237)$$

In the final form, the thermal EOS for carbon dioxide is represented by Eq. (228) with the coefficients determined by Eqs. (229) and (231)–(233).

It is worth to present the other (equivalent) forms of Eq. (228). If pressure, density and temperature are taken in MPa,  $\text{kg/m}^3$ , and K, respectively, then

$$p = \rho R_g T[1 + B_g \rho + (b_g \rho)^2 + (b_g \rho)^3], \quad (238)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad b_g = b/\mu, \quad (239)$$

and

$$\mu = 44.011 \text{ g/mol}.$$

In terms of dimensionless variables

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c \quad (240)$$

(values of critical parameters are given above by Eqs. (226), (230), and (237)), Eq. (228) can be transformed to

$$\Pi = Z_c^{-1} r \tau [1 + \bar{B}r + (\bar{b}r)^2 + (\bar{b}r)^3], \quad (241)$$

where

$$\bar{B} \equiv B \rho_c, \quad (242)$$

$$Z_c \equiv p_c/(\rho_c R T_c) = 0.27467, \quad (243)$$

$$\bar{b} \equiv b \rho_c \equiv \lambda/Z_c = 0.41869. \quad (244)$$

To check the accuracy of Eq. (228) (as well as equivalent Eqs. (238) and (241)), comparison with available data [49] at  $p < 20 \text{ MPa}$  and  $280 \text{ K} \leq T \leq 1273 \text{ K}$  has been made along 14 isotherms, which is presented in Table 28.

Table 28 shows that EOS (228) (and equivalent Eqs. (238) and (241)) provides the accuracy better than 0.1% at  $p \leq 20 \text{ MPa}$  and  $280 \leq T \leq 1500 \text{ K}$ . For isotherm  $T = 1500 \text{ K}$  comparison is made with tables [2]. In general, agreement of predicted pressure with tabulated values in [2] is somewhat worse and the maximum error is 0.4%. As mentioned in Section 6.1, the tabulated pressure (at given density and temperature) in [49] is systematically lower than the tabulated pressure in [2, 39] under similar conditions. Therefore the maximal error of 0.4% can be caused by the error inherent in the tables. Anyway, it is important to note that discrepancy between the predictions and tabulated data is within the accuracy of tabulated data.

At relatively low temperatures (10–150°C) Table 28 shows only the data for pressures below 20 MPa. At higher pressures, the accuracy of EOS (228) becomes significantly worse. This is caused by the proximity to the critical point and high values of relative density  $\rho/\rho_c$ . This parametric domain, where temperatures are low and pressures are high is virtually of no interest for CFD applications dealing with piston engines.

### 6.3. Equation of State in the Form of Virial Series for Carbon Dioxide

The EOS in the form of Eq. (228), (as well as Eq. (238) or Eq. (241)) with constant  $\lambda$  has the form of truncated virial series with four terms. Introducing notations:

$$\bar{C} = \bar{b}^2, \quad \bar{D} = \bar{b}^3 \quad (245)$$

**Table 28.** Comparison of predictions given by Eq. (228) with tabulated data [49] and [2] along 14 isotherms

Isotherm $t = 10^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
9.640	0.5015	0.5	0.30
19.93	1.006	1	0.57
43.02	2.022	2	1.1
70.98	3.043	3	1.4
107.93	4.053	4	1.3
Isotherm $t = 40^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
8.638	0.5008	0.5	0.16
17.677	1.003	1	0.30
37.16	2.012	2	0.60
58.94	3.021	3	0.70
83.82	4.025	4	0.63
113.08	5.011	5	0.23
149.15	5.954	6	0.82
Isotherm $t = 70^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
7.837	0.5005	0.5	0.10
15.934	1.0020	1	0.20
32.90	2.0017	2	0.085
51.35	3.012	3	0.4
71.25	4.015	4	0.38
92.99	5.011	5	0.22
116.97	5.993	6	0.11
173.8	7.870	8	1.6
Isotherm $t = 100^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
7.177	0.5003	0.5	0.06
14.529	1.0012	1	0.12
29.79	2.004	2	0.21
45.86	3.008	3	0.26
62.81	4.010	4	0.24
80.74	5.008	5	0.17
99.75	6.001	6	0.019
141.47	7.957	8	0.54
Isotherm $t = 150^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
12.696	1.0006	1	0.08
25.78	2.002	2	0.12
39.25	3.003	3	0.11
53.14	4.005	4	0.12
67.45	5.005	5	0.09
82.00	6.003	6	0.05
113.03	7.991	8	0.11
145.62	9.962	10	0.38
179.9	11.91	12	0.75

**Table 28.** (Contd.)

Isotherm $t = 200^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
11.291	1.0002	1	0.02
22.79	2.0008	2	0.04
34.50	3.0016	3	0.055
46.42	4.0025	4	0.06
58.54	5.0025	5	0.05
70.86	6.0016	6	0.03
96.10	7.998	8	0.025
122.07	9.989	10	0.11
148.69	11.975	12	0.21
175.8	13.953	14	0.34
203.3	15.93	16	0.47
231.0	17.89	18	0.59
258.7	19.86	20	0.70
Isotherm $t = 250^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
20.47	2.0001	2	0.04
30.87	3.001	3	0.01
41.37	4.0005	4	0.01
51.98	5.0006	5	0.01
62.69	6.0006	6	0.01
84.38	7.9997	8	0.00
106.39	9.998	10	0.02
128.65	11.994	12	0.05
151.10	13.99	14	0.07
173.7	15.99	16	0.06
196.2	17.98	18	0.11
218.7	19.98	20	0.10
Isotherm $t = 300^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
56.42	6.000	6	0.00
75.59	8.000	8	0.01
94.89	10.000	10	0.00
114.26	12.000	12	0.00
133.67	14.001	14	0.01
153.09	16.006	16	0.04
172.4	18.009	18	0.05
191.6	20.014	20	0.07
Isotherm $t = 400^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
47.28	5.999	6	0.02
63.04	7.999	8	0.01
78.76	10.000	10	0.00
94.42	12.001	12	0.01
110.01	14.004	14	0.03
125.5	16.008	16	0.05
140.88	18.015	18	0.09
156.13	20.025	20	0.13



Table 28. (Contd.)

Isotherm $t = 500^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
40.85	5.999	6	0.02
54.34	7.999	8	0.01
67.74	9.999	10	0.01
81.05	12.000	12	0.00
94.26	14.002	14	0.02
107.35	16.005	16	0.03
120.33	18.010	18	0.06
133.17	20.016	20	0.08
Isotherm $t = 600^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
47.88	8.000	8	0.00
59.62	9.999	10	0.01
71.27	12.000	12	0.00
82.81	14.001	14	0.01
94.24	16.003	16	0.02
105.55	18.005	18	0.03
116.74	20.008	20	0.04
Isotherm $t = 800^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
38.81	8.001	8	0.01
48.30	10.001	10	0.01
57.69	11.999	12	0.01
67.00	14.000	14	0.00
76.20	15.998	16	0.02
85.32	17.998	18	0.01
94.33	19.996	20	0.02
Isotherm $t = 1000^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
32.70	8.002	8	0.02
40.69	10.001	10	0.01
48.61	12.001	12	0.01
56.44	13.997	14	0.02
64.21	15.997	16	0.02
71.89	17.994	18	0.04
79.50	19.991	20	0.04
Isotherm $t = 1500^{\circ}\text{C}$			
$\rho$ , g/cm <sup>3</sup>	$p$ , MPa, calc. Eq. (228)	$p_1$ , MPa, data [49]	$ p_1 - p /p_1$ , %
2.498	6.996	7	0.06
3.567	9.996	10	0.04
14.16	39.93	40	0.18
24.59	69.78	70	0.32
34.87	99.59	100	0.41

**Table 29.** Specific heat  $C_{p0}$  of carbon dioxide in the ideal-gas state and the accuracy of approximation given by Eqs. (256) and (257)

$T, \text{ K}$	$C_p/R$ [49]	$C_{p0}/R$ , Eqs. (256), (257)	$ \delta C_{p0} /C_{p0}$ , %
280	4.3643	4.3653	0.023
290	4.4208	4.4213	0.011
300	4.4763	4.4762	-0.002
350	4.7371	4.7343	-0.059
400	4.9704	4.9657	-0.095
450	5.1792	5.1737	-0.106
500	5.3671	5.3618	-0.099
600	5.6915	5.6883	-0.056
700	5.9611	5.9604	-0.012
800	6.186	6.1873	0.021
900	6.3742	6.371	-0.050
1000	6.5318	6.5362	0.067
1200	6.776	6.7815	0.081
1400	6.952	6.9575	0.079
1600	7.082	7.0862	0.069
1800	7.18	7.1848	0.067
2000	7.258	7.2608	0.039
2200	7.32	7.3214	0.019
2400	7.371	7.3708	-0.003
2600	7.414	7.4119	-0.028
2800	7.451	7.4469	-0.055
3000	7.484	7.4771	-0.092

(where  $\bar{b} = 0.27467$ , see Eq. (244)) one obtains from Eq. (241):

$$\Pi = r\tau/Z_c(1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (246)$$

where  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$  are the dimensionless virial coefficients. Note that at constant  $\lambda$  coefficients  $\bar{C}$  and  $\bar{D}$  are independent of temperature. As a consequence, the calculation of thermodynamic functions is simplified considerably (see Section 6.4).

For the sake of convenience, we provide below two other versions of the EOS with the explicit record of the third and fourth terms of the virial series.

If pressure, density, and temperature are taken in MPa, kmol/m<sup>3</sup>, and K, respectively, one has

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3) \text{ with} \quad (247)$$

$$R = 0.00831434 \text{ kJ/(mol K)},$$

where

$$C \equiv b^2, \quad D \equiv b^3, \quad (248)$$

and parameter  $b$  is given by Eqs. (229) and (231).

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, one obtains:

$$p = \rho R_g T(1 + B_g \rho + C_g \rho^2 + D_g \rho^3), \quad (249)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad C_g = C/\mu^2, \quad (250)$$

$$D_g = D/\mu^3,$$

and  $\mu = 44.011 \text{ g/mol}$ .

#### 6.4. First and Second Derivatives of Virial Coefficients for Carbon Dioxide

Because parameter  $\lambda$  entering the EOS of carbon dioxide is independent of temperature, the derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore, one has to derive formulae for the derivatives of the second virial coefficient only. These derivatives can be derived by differentiating Eq. (236). Introducing notation

$$\bar{B} = \left( \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i} \right) s \quad (251)$$

with  $s$  given by Eq. (232), one obtains:

**First logarithmic derivative,  $\bar{B}_1$ :**

$$\bar{B}_1 \equiv \tau \frac{d\bar{B}}{d\tau} = - \left( \sum_{i=1,2,3,8} i \bar{A}_i \tau^{-i} \right) s + s_1 \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i}, \quad (252)$$

where

$$s_1 \equiv \tau \frac{ds}{d\tau} = 0.75983 \tau \exp(-1.55726 \tau). \quad (253)$$

**Second logarithmic derivative,  $\bar{B}_2$ :**

$$\bar{B}_2 \equiv \tau \frac{d\bar{B}_1}{d\tau} = s \left( \sum_{i=1,2,3,8} i^2 \bar{A}_i \tau^{-i} \right) - 2s_1 \sum_{i=1,2,3,8} i \bar{A}_i \tau^{-i} + s_2 \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i}, \quad (254)$$

where

$$s_2 \equiv \tau \frac{ds_1}{d\tau} = 0.75983 \tau (1 - 1.55726 \tau) \exp(-1.55726 \tau). \quad (255)$$

#### 6.5. Accuracy of Thermal Equation of State at Temperatures Exceeding 1500 K

At temperatures exceeding 1500 K gas density is relatively low even at pressure of 20 MPa. Therefore at  $T > 1500 \text{ K}$  and  $p \leq 20 \text{ MPa}$  the accuracy of the virial

EOS is mainly determined by the accuracy of the second virial coefficient. Equation (225) for the second virial coefficient was obtained for entire temperature range:  $280\text{ K} \leq T \leq 3000\text{ K}$ . Good agreement of predicted and tabulated pressure values at temperatures below  $1500\text{ K}$  and sufficiently wide range of applicability of Eq. (225) in terms of temperature allow one to believe that Eq. (228) provides satisfactory accuracy at  $1500\text{ K} < T < 3000\text{ K}$ , being at the level not worse than 1%.

#### 6.6. Calculation of Density or Temperature Based on Other Two Variables of Thermal Equation of State

The EOS (228) provides explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively (see Section 1.5).

#### 6.7. Ideal-Gas Specific Heats and Thermodynamic Functions for Carbon Dioxide

For carbon dioxide, detailed tabulated data on the ideal-gas specific heat  $C_{p0}$  within entire required temperature range  $280\text{ K} \leq T \leq 3000\text{ K}$  are presented in [2, 39, 49–51]. The tabulated data are taken mainly from the same references and are either identical or differ insignificantly. In handbook [49], a comparative analysis of available data on  $C_{p0}$  has been made and preference has been given to Wooley's data [51] due to simultaneous coverage of low and high temperatures and detailed list of thermodynamic functions of carbon dioxide in the ideal-gas state. A part of tabulated data for  $C_{p0}$ , presented in [49] (pp. 240, 241) is reproduced here in Table 29 for the temperature range  $280\text{ K} \leq T \leq 3000\text{ K}$ .

Available analytical approximations of  $C_{p0}$  for carbon dioxide are either related to a limited temperature range [6], out of which their accuracy is getting poor, or represent a set of lumped approximations. We have obtained the other approximation, which overcomes these drawbacks and is similar to that used for other individual substances. The ideal-gas specific heat  $C_{p0}$  was represented as a sum of two terms: the ideal-gas specific heat in harmonic approximation for molecular vibrations and small correction  $\delta C_{p0}$  allowing for analytical integration. The resultant formula for the ideal-gas molar specific heat is as follows:

$$C_{p0}/R = 7/2 + \sum_{i=1}^4 x_i^2 \exp(x_i)/[\exp(x_i) - 1]^2 + \delta C_{p0}/R \quad (256)$$

with

$$\delta C_{p0}/R = -0.00337 + 4.43 \times 10^{-5} T \quad (257)$$

or

$$\delta C_{p0} = -0.02802 + 3.6833 \times 10^{-4} T \text{ J/(mol K)}, \quad (258)$$

where  $x_i = \theta_i/T$ ;  $\theta_1 = 3380\text{ K}$ ,  $\theta_2 = 1995\text{ K}$ ,  $\theta_3 = \theta_4 = 960\text{ K}$  are the characteristic vibration temperatures of carbon dioxide molecule [31], and  $T$  is temperature in K. Correction  $\delta C_{p0}$  was obtained by linear approximation of the difference between the tabulated data of  $C_{p0}$  from [49] (see second column in Table 29) and the value

$$7/2 + \sum_{i=1}^4 x_i^2 \exp(x_i)/[\exp(x_i) - 1]^2$$

in the temperature range  $280\text{ K} \leq T \leq 3000\text{ K}$ . The results of calculation of  $C_{p0}$  by using Eqs. (256) and (257) and their discrepancy from the reference data are presented in the third and fourth columns of Table 29.

As follows from Table 29, the approximation error of  $C_{p0}$  by Eqs. (256) and (257) is less than 0.1% within the entire temperature range of interest. This error is of the same order as the error of the tabulated data.

Integration of Eqs. (256) and (257) gives for the molar enthalpy (with reference temperature  $T = 0\text{ K}$ ) in the ideal-gas state:

$$H_0/R = 3.49663 T + 2.215 \times 10^{-5} T^2 + \sum_{i=1}^4 \theta_i/[\exp(\theta_i/T) - 1]. \quad (259)$$

The units of  $C_{p0}$  and  $H_0$  depend on the choice of units for the universal gas constant  $R$ . For example, to obtain  $C_{p0}$  and  $H_0$  in J/(mol K) and J/mol, respectively, one has to use in Eqs. (256) and (257) the value of  $R$  equal to  $R = 8.31434$  (8.314510) J/(mol K). To obtain  $C_{p0}$  and  $H_0$  in J/(g K) and J/g, respectively, one has to use instead of  $R$  the value of  $R/\mu$  with  $\mu = 44.011\text{ g/mol}$  in Eqs. (256) and (258), i.e.,

$$R_g \equiv R/\mu = 0.188915 \text{ J/(g K)}. \quad (260)$$

The specific heats  $C_{p0}$  and  $C_{v0}$  are related to each other via the well-known thermodynamic relationships (40) or (41). The corresponding relationships between the enthalpy and the internal energy are given by Eqs. (91) or (92).

The ideal-gas entropy of carbon dioxide is given by the relationship:

$$S_0/R = \int_{T_0}^T \frac{C_{p0}}{RT} dT = 3.496633 \ln(T/T_0) + 4.43 \times 10^{-5} (T - T_0) + S_{vib}/R + \text{Const}(T_0), \quad (261)$$

where  $T_0$  is the reference temperature, for example,  $298.15\text{ K}$ , and  $S_{vib}$  is the vibration component of

**Table 30.** Second virial coefficient for hydrogen [50]

$T, K$	293.15	298.15	400	500	600	700	800
$B, 10^{-3} \text{ dm}^3/\text{mol}$ [50]	12.16	12.34	14.36	14.98	15.66	16.38	16.68
$T, K$	900	1000	1200	1400	1600	1800	2000
$B, 10^{-3} \text{ dm}^3/\text{mol}$ [50]	16.70	16.72	16.69	16.55	16.39	16.22	16.06
$T, K$	2200	2400	2600	2800	3000		
$B, 10^{-3} \text{ dm}^3/\text{mol}$ [50]	15.86	15.69	15.52	15.37	15.22		

entropy (harmonic oscillator) equal to

$$S_{vib}/R = \sum_{i=1}^4 \left[ \ln \frac{\exp(x_{i0}) - 1}{\exp(x_i) - 1} + \frac{x_i}{1 - \exp(-x_i)} - \frac{x_{i0}}{1 - \exp(-x_{i0})} \right], \quad (262)$$

where  $x_{i0} = \theta_i/T_0$ . Similar to the specific heats, the units of entropy are chosen depending on the units of  $R$ .

### 6.8. Excess Thermodynamic Functions and Excess Specific Heats for Carbon Dioxide

Due to the fact that coefficient  $\lambda$  in the thermal EOS of carbon dioxide is independent of temperature, the first and second derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore all excess thermodynamic functions are related only to the derivatives of the second virial coefficient.

The excess internal energy for carbon dioxide is given by

$$E_{exc}/(RT) = -\bar{B}_1 r = -B_1 \rho, \quad (263)$$

where index 1 at virial coefficient denotes first logarithmic derivative  $B_1 \equiv Td\bar{B}/dT$ , or in dimensionless form,  $\bar{B}_{11} \equiv \tau d\bar{B}/d\tau$ . This derivative is given explicitly by Eqs. (252), (253).

Differentiation of Eq. (263) with respect to temperature gives the expression for the excess specific heat at constant volume:

$$C_{v,exc}/R = -(\bar{B}_1 + \bar{B}_2)r, \quad (264)$$

where index 2 at virial coefficient denotes the second logarithmic derivative  $\bar{B}_2 \equiv \tau d\bar{B}_1/d\tau$ . This derivative is given explicitly by Eqs. (254), (255).

The excess enthalpy  $H_{exc}$  relates to the excess internal energy and the excess pressure as in Eq. (51) with

$$p_{exc}/\rho = (p - p_{id})/\rho = RT_c \tau (\bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (265)$$

and  $p_{id}$  is the ideal-gas pressure. Coefficient  $\bar{B}$  is given by Eq. (236) or (242). Coefficients  $\bar{C}$  and  $\bar{D}$  are calculated by Eqs. (245).

If  $H_{exc}$  and  $E_{exc}$  are taken in kJ/mol, then pressure, density, and temperature in Eq. (265) should be taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively.

In this case, the universal gas constant is taken in kJ/(mol K) and is equal to  $R = 0.00831434 \text{ kJ}/(\text{mol K})$ .

Differentiation of Eq. (51) with respect to temperature gives the expression for the excess specific heat at constant pressure:

$$C_{p,exc}/R = C_{v,exc}/R + \bar{B}_s r + \bar{C}r^2 + \bar{D}r^3, \quad (266)$$

where

$$\bar{B}_s \equiv d(\tau \bar{B})/d\tau \equiv \bar{B} + \bar{B}_1. \quad (267)$$

The excess entropy can be calculated using  $p$ – $\rho$ – $T$  EOS and Eq. (55). Substituting the EOS (246) in the integral of Eq. (55) gives

$$\begin{aligned} & \int_0^{\rho} [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \\ &= -R \int_0^r (\bar{B}_s + \bar{C}r + \bar{D}r^2) dr, \end{aligned} \quad (268)$$

where the coefficient with index  $s$  is defined by Eq. (267). Taking the integral in the right-hand-side of Eq. (268) allows rewriting of Eq. (55) in the final form:

$$S_{exc}/R = -\ln\left(\frac{\rho RT}{0.101325}\right) - (\bar{B}_s r + \bar{C}r^2/2 + \bar{D}r^3/3), \quad (269)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434 \text{ kJ}/(\text{mol K})$ .

### 6.9. Thermodynamic Functions and Specific Heats for Carbon Dioxide

Internal energy, enthalpy, specific heat at constant volume,  $C_v$ , specific heat at constant pressure,  $C_p$ , and entropy can be calculated using Eqs. (58)–(62). The thermal EOS (228) together with the equation for internal energy (58) or enthalpy (59) determines the parametric relationships  $p$ – $\rho$ – $E$  or  $p$ – $\rho$ – $H$ , respectively, with temperature serving as a parameter.

## CHAPTER 7: HYDROGEN

### 7.1. Second Virial Coefficient in the Equation of State for Hydrogen

For obtaining the EOS for molecular hydrogen the approach developed in Chapter 1 has been also applied. The thermal EOS in the form of explicit

dependence of pressure  $p$  on density  $\rho$  and temperature  $T$  has been obtained for temperature range from 280 to 3000 K and pressure up to 20 MPa.

The data on the second virial coefficient of hydrogen up to temperature of 3000 K are reported in [50] and reproduced here in Table 30.

Similar to other species of interest, to obtain the analytical approximation for the second virial coefficient we used the following formula:

$$B = A_0 + A_1/\tau + A_2/\tau^2 + A_3/\tau^3 + A_8/\tau^8 \text{ dm}^3/\text{mol}, \quad (270)$$

where  $\tau \equiv T/T_c$ , and  $T_c$  is equal to [52]:

$$T_c = 33.23 \text{ K}. \quad (271)$$

The values of coefficients  $A_0, A_1, \dots, A_8$  in Eq. (270) were determined by nonlinear regression analysis based on  $B$  values of Table 30 (dimension  $\text{dm}^3/\text{mol}$ ):

$$\begin{aligned} A_0 &= 0.0127441, & A_1 &= 0.293802, & A_2 &= -6.49817, \\ A_3 &= 39.5001, & A_8 &= -2.94127 \times 10^5. \end{aligned} \quad (272)$$

Comparison of the approximation given by Eqs. (270), (272) with the data of Table 30 is shown in Fig. 10.

## 7.2. Thermal Equation of State for Hydrogen

Tabulated  $p$ – $v$ – $T$ -data for hydrogen are reported in handbook [52] for temperatures up to 1500 K and pressures up to 100 MPa, and in [53] for the temperature range  $500 \text{ K} \leq T \leq 2500 \text{ K}$  and pressure up to 80–350 MPa (the upper pressure limit depends on temperature: at  $T = 500 \text{ K}$  it is 80 MPa, at  $T = 2500 \text{ K}$  it is 350 MPa). In the overlapping range of  $p$ – $v$ – $T$ -parameters, the data of [52] and [53] agree with each other within hundredth fractions of percent.

Our objective was to construct a simple EOS possessing accuracy, which is sufficient for CFD applications at temperatures and pressures ranging from 280 to 3000 K and up to 20 MPa, respectively. To implement this objective, we applied the methodology of Chapter 1 and Eqs. (270), (272) as a first approximation for the second virial coefficient  $B$ . Later on, when determining the parameters of the thermal EOS based on  $p$ – $v$ – $T$  tables of [52], the coefficients given by Eq. (272) were corrected (see Eqs. (277) and (278) below).

The EOS is taken in the form:

$$p = \rho RT[1 + B\rho + b^2\rho^2 + b^3\rho^3], \quad (273)$$

$$b = \lambda RT_c/p_c \quad (274)$$

with  $p_c$  equal to [52]:

$$p_c = 1.316 \text{ MPa} \quad (275)$$

and  $\lambda$  given by the approximation

$$\lambda = \text{const} = 0.1161. \quad (276)$$

To obtain better accuracy at low temperatures, we corrected the expression (270) for the second virial coef-

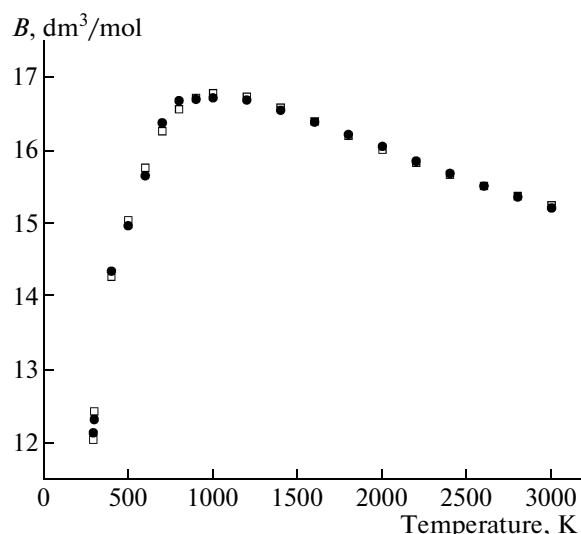


Fig. 10. Second virial coefficient for hydrogen. Circles correspond to tabulated data [50] (see Table 30). Squares correspond to approximation of Eqs. (270), (272).

ficient by multiplying the right-hand-side of Eq. (270) by coefficient  $s$  depending on temperature as

$$s = 1 + 9.67017 \times 10^8 \exp(-T/12.493), \quad (277)$$

where  $T$  is taken in Kelvin. This allowed us to attain better agreement of predictions based on Eq. (273) with tabulated data [52] at low temperatures (280–300 K). The corrected expression for the second virial coefficient is now given as

$$B = (A_0 + A_1/\tau + A_2/\tau^2 + A_3/\tau^3 + A_8/\tau^8)s \text{ dm}^3/\text{mol}, \quad (278)$$

where coefficients  $A_0, A_1, \dots, A_8$  are defined by Eqs. (272). In terms of dimensionless variables

$$\bar{B} = (\bar{A}_0 + \bar{A}_1/\tau + \bar{A}_2/\tau^2 + \bar{A}_3/\tau^3 + \bar{A}_8/\tau^8)s, \quad (279)$$

where  $A_i = A_i \rho_c$ ,  $i = 0, 1, 2, 3$ , and 8, and  $\rho_c$  is equal to [52]:

$$\rho_c = 15.377 \text{ mol/dm}^3. \quad (280)$$

In the final form, the thermal EOS for hydrogen is represented by Eq. (273) with the coefficients determined by Eqs. (274), (276), (277), and (278).

It is worth to present the other (equivalent) forms of Eq. (273). If pressure, density and temperature are taken in MPa,  $\text{kg/m}^3$ , and K, respectively, then

$$p = \rho R_g T[1 + B_g \rho + (b_g \rho)^2 + (b_g \rho)^3], \quad (281)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad b_g = b/\mu, \quad (282)$$

and  $\mu = 2.016 \text{ g/mol}$ .

In terms of dimensionless variables

$$\Pi \equiv p/p_c, \quad \tau \equiv T/T_c, \quad r \equiv \rho/\rho_c \quad (283)$$

**Table 31.** Comparison of predictions given by Eq. (273) with tabulated data [52, 53]

Isotherm $T = 280$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
1.74279	3.998	4	0.05
2.61978	5.994	6	0.10
3.49509	7.990	8	0.13
4.36502	9.986	10	0.14
5.22381	14.990	15	0.07
6.06411	20.03	20	0.15
Isotherm $T = 300$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
1.6149	3.998	4	0.05
2.41981	5.994	6	0.10
3.21878	7.990	8	0.13
4.00928	9.986	10	0.14
4.78791	14.990	15	0.07
5.55036	20.03	20	0.15
Isotherm $T = 350$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
1.36891	3.998	4	0.05
2.04203	5.994	6	0.10
2.70506	7.990	8	0.13
3.35702	9.986	10	0.14
3.99687	14.990	15	0.07
4.62332	20.03	20	0.15
Isotherm $T = 400$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
1.19093	3.998	4	0.05
1.77288	5.994	6	0.10
2.34427	7.990	8	0.13
2.90469	9.986	10	0.14
3.45382	14.990	15	0.07
3.99131	20.03	20	0.15
Isotherm $T = 500$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
0.94818	3.998	4	0.05
1.40962	5.994	6	0.10
1.86196	7.990	8	0.13
2.30518	9.986	10	0.14
2.73932	14.990	15	0.07
3.16448	20.03	20	0.15

Table 31. (Contd.)

Isotherm $T = 600$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
0.78916	3.998	4	0.05
1.17315	5.994	6	0.10
1.54979	7.990	8	0.13
1.91912	9.986	10	0.14
2.28124	14.990	15	0.07
2.63631	20.03	20	0.15
Isotherm $T = 700$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
0.67642	3.998	4	0.05
1.00590	5.994	6	0.10
1.32943	7.990	8	0.13
1.64706	9.986	10	0.14
1.95891	14.990	15	0.07
2.26509	20.03	20	0.15
Isotherm $T = 800$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
0.59215	3.998	4	0.05
0.88099	5.994	6	0.10
1.16494	7.990	8	0.13
1.44407	9.986	10	0.14
1.71846	14.990	15	0.07
1.98822	20.03	20	0.15
Isotherm $T = 1000$ K			
$\rho$ , mol/dm <sup>3</sup>	$p$ , MPa, calc. Eq. (273)	$p_1$ , MPa, data [52]	$ p_1 - p /p_1$ , %
0.78399	5.994	6	0.10
1.03720	7.990	8	0.13
1.28640	9.986	10	0.14
1.53166	14.990	15	0.07
1.77307	20.03	20	0.15

(values of critical parameters are given above by Eqs. (271), (275), and (280)), Eq. (273) can be transformed to

$$\Pi = Z_c^{-1} r \tau [1 + \bar{B}r + (\bar{b}r)^2 + (\bar{b}r)^3], \quad (284)$$

where

$$\bar{B} \equiv B p_c, \quad (285)$$

$$Z_c \equiv p_c / (\rho_c R T_c) = 0.30387, \quad (286)$$

$$\bar{b} \equiv b p_c \equiv \lambda / Z_c = 0.3820. \quad (287)$$

To check the accuracy of Eq. (273) (as well as equivalent Eqs. (280) and (284)), comparison with available

data [52, 53] at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 2500 \text{ K}$  has been made along several isotherms. Some examples for the temperature range 280–1000 K are presented in Table 31.

The obtained results show that in general EOS (273) (and equivalent Eqs. (280) and (284)) provides the accuracy better than hundredth fractions of percent at  $p \leq 20$  MPa and  $280 \text{ K} \leq T \leq 2500 \text{ K}$  with the maximum error of 0.5% attained in several points at low temperatures and high pressure close to 20 MPa. Keeping in mind that compression in piston engines results in a significant temperature rise and “cold” compression is of no interest for such applications, the

accuracy of Eq. (273) should be treated as very good. It is also important to note that discrepancy between the predictions and the tabulated data of [52, 53] is within the accuracy of the tabulated data.

### 7.3. Equation of State in the Form of Virial Series for Hydrogen

The EOS in the form of Eq. (273) (as well as Eq. (281) or Eq. (284)) with constant  $\lambda$  has the form of truncated virial series with four terms. Introducing notations:

$$\bar{C} = \bar{b}^2, \quad \bar{D} = \bar{b}^3 \quad (288)$$

(where  $\bar{b} = 0.3820$ , see Eq. (287)) one obtains from Eq. (284):

$$\Pi = r\tau/Z_c(1 + \bar{B}r + \bar{C}r^2 + \bar{D}r^3), \quad (289)$$

where  $\bar{B}$ ,  $\bar{C}$ , and  $\bar{D}$  are the dimensionless virial coefficients determined by Eqs. (279) and (288). Note that at constant  $\lambda$  coefficients  $\bar{C}$  and  $\bar{D}$  are independent of temperature. As a consequence, the calculation of thermodynamic functions is simplified considerably (see Section 7.4 below).

For the sake of convenience, we provide below two versions of the EOS with explicit record of the third and fourth terms of the virial series.

If pressure, density, and temperature are taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively, one has

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3) \quad \text{with} \quad (290)$$

$$R = 0.00831434 \text{ kJ}/(\text{mol K}),$$

where

$$C \equiv b^2, \quad D \equiv b^3, \quad (291)$$

and parameter  $b$  is given by Eq. (274).

If pressure, density and temperature are taken in MPa, kg/m<sup>3</sup>, and K, respectively, one obtains:

$$p = \rho R_g T(1 + B_g \rho + C_g \rho^2 + D_g \rho^3), \quad (292)$$

where

$$R_g = R/\mu, \quad B_g = B/\mu, \quad C_g = C/\mu^2, \quad (293)$$

$$D_g = D/\mu^3.$$

### 7.4. First and Second Derivatives of Virial Coefficients for Hydrogen

Because parameter  $\lambda$  entering the EOS of hydrogen is independent of temperature, the derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore, one has to derive formulae for the derivatives of the second

virial coefficient only. These derivatives can be derived by differentiating Eq. (279). Introducing notation

$$\bar{B} = \left( \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i} \right) s \quad (294)$$

with  $s$  given by Eq. (277), one obtains:

**First logarithmic derivative,  $\bar{B}_1$ :**

$$\bar{B}_1 \equiv \tau \frac{d\bar{B}}{d\tau} = - \left( \sum_{i=1,2,3,8} i \bar{A}_i \tau^{-i} \right) s + s_1 \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i}, \quad (295)$$

where

$$s_1 \equiv \tau \frac{ds}{d\tau} = -2.57216 \times 10^9 \tau \exp(-2.6599\tau). \quad (296)$$

**Second logarithmic derivative,  $\bar{B}_2$ :**

$$\bar{B}_2 \equiv \tau \frac{d\bar{B}_1}{d\tau} = s \left( \sum_{i=1,2,3,8} i^2 \bar{A}_i \tau^{-i} \right) - 2s_1 \sum_{i=1,2,3,8} i \bar{A}_i \tau^{-i} + s_2 \sum_{i=0,1,2,3,8} \bar{A}_i \tau^{-i}, \quad (297)$$

where

$$s_2 \equiv -2.57216 \times 10^9 \tau (1 - 2.6599\tau) \times \exp(-2.6599\tau). \quad (298)$$

### 7.5. Accuracy of Thermal Equation of State at Temperatures Exceeding 2500 K

At temperatures exceeding 2500 K, gas density is relatively low even at pressure of 20 MPa. Therefore at  $T > 2500$  K and  $p \leq 20$  MPa the accuracy of the virial EOS is mainly determined by the accuracy of the second virial coefficient. Equations (270) and (272) for the second virial coefficient were obtained for temperatures  $T \leq 3000$  K. Good agreement of predicted and tabulated pressures at temperatures below 2500 K and better (in average) accuracy of predicted pressure at higher temperatures (see Table 31) allow one to believe that accuracy of Eq. (273) at  $2500 \text{ K} \leq T \leq 3000 \text{ K}$  will not be worse than at  $280 \text{ K} \leq T \leq 2500 \text{ K}$ .

### 7.6. Calculation of Density or Temperature Based on Other Two Variables of Thermal Equation of State

The EOS of Eq. (273) provides explicitly the value of pressure  $p$  at given values of temperature  $T$  and density  $\rho$ . In cases, when there is a need of determining density  $\rho$  at given values of  $p$  and  $T$ , or determining temperature  $T$  at given values of  $\rho$  and  $p$ , this task is solved iteratively (see Section 1.5).



### 7.7. Ideal-Gas Specific Heats and Thermodynamic Functions for Hydrogen

For hydrogen, detailed tabulated data on the ideal-gas specific heat  $C_{p0}$  are presented elsewhere [2, 39] for temperatures up to 1100 K and in handbook [50] up to 2000 K. A part of the tabulated data from [50] is reproduced here in Table 32 for temperatures ranging from 280 to 3000 K. The analytical approximation of tabulated data [2] in the temperature range from 60 to 1400 K is reported in [6].

We did not find a sufficiently precise approximation for  $C_{p0}$  for hydrogen for the entire temperature range from 280 to 3000 K. In [6], a third-order temperature polynomial is used to approximate  $C_{p0}$  for hydrogen. However, this approximation is valid only at  $T < 1500$  K. Therefore we have obtained the other approximation, which is sufficiently accurate, valid for the entire temperature range of interest, and allows for simple analytical integration. To do so, the ideal-gas specific heat was represented as a sum of two terms: the ideal-gas specific heat in harmonic approximation for molecular vibrations and small correction  $\Delta$  in the form of first-order temperature polynomial. The resultant formula for the ideal-gas molar specific heat is as follows:

$$C_{p0}/R = 7/2 + x^2 \exp(x)/[\exp(x) - 1]^2 + \Delta \quad (299)$$

with

$$\Delta = -0.040955 + 1.006213 \times 10^{-4} T, \quad (300)$$

280 K  $\leq T \leq$  3000 K,

where  $x = \theta/T$ ,

$$\theta = 6323.26 \text{ K} \quad (301)$$

is the characteristic vibration temperature of hydrogen molecule [31], and  $T$  is temperature in K. The results of calculation of  $C_{p0}$  using Eqs. (299) and (300) and their discrepancy from the reference data are presented in Table 32. As follows from Table 32, the approximation error of  $C_{p0}$  given by Eqs. (299) and (300) is less than 0.14% within the entire temperature range of interest. This error is of the same order as the error of tabulated data.

Integration of Eqs. (299) and (300) gives the expression for the molar enthalpy (with reference temperature  $T = 0$  K) in ideal-gas state:

$$H_0/R = 3.45905 T + 5.03107 \times 10^{-5} T^2 + \theta/[\exp(\theta/T) - 1]. \quad (302)$$

The units of  $C_{p0}$  and  $H_0$  depend on the choice of units for the universal gas constant  $R$ . For example, to obtain  $C_{p0}$  and  $H_0$  in J/(mol K) and J/mol, respectively, one has to use in Eqs. (299) and (302) the value of  $R = 8.31434$  J/(mol K). To obtain  $C_{p0}$  and  $H_0$  in J/(g K) and J/g, respectively, one has to use the value of  $R/\mu$  with  $\mu = 2.016$  g/mol instead of  $R$  in Eqs. (299) and (302), i.e.,

$$R_g \equiv R/\mu = 4.12418 \text{ J/(g K)}. \quad (303)$$

**Table 32.** Accuracy of approximation for  $C_{p0}$  given by Eqs. (299) and (300)

$T$ , K	$C_p$ , J/(mol K) Eq. (300)	$C_{p0}$ , J/(mol K) [2]	$\delta C_{p0}/C_{p0}$ , %
298.15	29.009	28.836	0.60
300	29.011	28.849	0.56
400	29.095	29.181	−0.30
500	29.182	29.260	−0.27
600	29.286	29.327	−0.14
700	29.426	29.440	−0.05
800	29.621	29.623	−0.01
900	29.878	29.880	−0.01
1000	30.195	30.204	−0.03
1100	30.561	30.580	−0.06
1200	30.964	30.991	−0.09
1300	31.389	31.422	−0.10
1400	31.825	31.860	−0.11
1500	32.262	32.296	−0.11
1600	32.692	32.724	−0.10
1700	33.111	33.138	−0.08
1800	33.515	33.535	−0.06
1900	33.902	33.915	−0.03
2000	34.271	34.277	−0.02
2100	34.623	34.622	0.00
2200	34.956	34.949	0.02
2300	35.273	35.259	0.04
2400	35.573	35.555	0.05
2500	35.858	35.837	0.06
2600	36.128	36.106	0.06
2700	36.385	36.363	0.06
2800	36.630	36.61	0.05
2900	36.863	36.847	0.04
3000	37.085	37.076	0.03

The specific heats  $C_{p0}$  and  $C_{v0}$  are related to each other via the well-known thermodynamic relationships (40) or (41). The corresponding relationships between enthalpy and internal energy are given by (91) or (92).

The ideal-gas entropy of hydrogen is given by the relationship:

$$S_0/R = \int_{T_0}^T \frac{C_{p0}}{RT} dT = 3.45905 \ln(T/T_0) + 1.00621 \times 10^{-4} (T - T_0) + S_{vib}/R + \text{Const}(T_0), \quad (304)$$

where  $T_0$  is the reference temperature, for example, 298.15 K, and  $S_{vib}$  is the vibration component of entropy (harmonic oscillator) equal to

$$\frac{S_{vib}}{R} = \ln \frac{\exp(x_0) - 1}{\exp(x) - 1} + \frac{x}{1 - \exp(-x)} - \frac{x_0}{1 - \exp(-x_0)}, \quad (305)$$

where  $x = \theta/T$ ,  $x_0 = \theta/T_0$ , and  $\theta = 6323.26$  K (see Eq. (301)). Similar to the specific heats, the units of entropy are chosen depending on the units of  $R$ .

### 7.8. Excess Thermodynamic Functions and Excess Specific Heats for Hydrogen

Due to the fact that coefficient  $\lambda$  in the thermal EOS for hydrogen is independent of temperature, the first and second derivatives of virial coefficients  $C$  and  $D$  are equal to zero. Therefore all excess thermodynamic functions are related only to the derivatives of the second virial coefficient. The excess internal energy for hydrogen is given by

$$E_{exc}/(RT) = -\bar{B}_1 r = -B_1 \rho, \quad (306)$$

where index 1 at virial coefficient denotes the first logarithmic derivative  $B_1 \equiv T dB/dT$ , or in dimensionless form,  $\bar{B}_1 \equiv \tau d\bar{B}/d\tau$ . This derivative is given explicitly by Eqs. (295), (296).

Differentiation of Eq. (306) with respect to temperature gives the expression for the excess specific heat at constant volume:

$$C_{v,exc}/R = -(\bar{B}_1 + \bar{B}_2)r, \quad (307)$$

where index 2 at virial coefficient denotes the second logarithmic derivative  $\bar{B}_2 \equiv \tau d\bar{B}_1/d\tau$ . This derivative is given explicitly by Eqs. (297), (298).

The excess enthalpy  $H_{exc}$  relates to the excess internal energy and the excess pressure as in Eq. (51) with

$$p_{exc}/\rho = (p - p_{id})/\rho = RT_c \tau (\bar{B}r + \bar{C}r^2 + \bar{D}r^3) \quad (308)$$

and  $p_{id}$  is the ideal-gas pressure. Coefficient  $\bar{B}$  is calculated by Eq. (294). Coefficients  $\bar{C}$  and  $\bar{D}$  are calculated by Eqs. (288).

If  $H_{exc}$  and  $E_{exc}$  are taken in kJ/mol, then pressure, density, and temperature in Eq. (308) should be taken in MPa, kmol/m<sup>3</sup> (or mol/dm<sup>3</sup>), and K, respectively. In this case, the universal gas constant is taken in kJ/(mol K) and is equal to  $R = 0.00831434$  kJ/(mol K).

Differentiation of Eq. (51) with respect to temperature gives the expression for the excess specific heat at constant pressure:

$$C_{p,exc}/R = C_{v,exc}/R + \bar{B}_s r + \bar{C}r^2 + \bar{D}r^3, \quad (309)$$

where

$$\bar{B}_s \equiv d(\tau \bar{B})/d\tau \equiv \bar{B} + \bar{B}_1. \quad (310)$$

The excess entropy can be calculated using  $p$ - $\rho$ - $T$  EOS and Eq. (55). Substituting the EOS (289) in the integral of Eq. (55) gives

$$\begin{aligned} & \int_0^\rho [\rho R - (\partial p / \partial T)_\rho] \rho^{-2} d\rho \\ &= -R \int_0^r (\bar{B}_s + \bar{C}r + \bar{D}r^2) dr. \end{aligned} \quad (311)$$

Taking the integral in the right-hand-side of Eq. (311) allows rewriting of Eq. (55) in the final form:

$$\begin{aligned} & S_{exc}/R \\ &= -\ln\left(\frac{\rho RT}{0.101325}\right) - (\bar{B}_s r + \bar{C}r^2/2 + \bar{D}r^3/3), \end{aligned} \quad (312)$$

where  $\rho$  is taken in mol/dm<sup>3</sup> and  $R = 0.00831434$  kJ/(mol K).

### 7.9. Thermodynamic Functions and Specific Heats for Hydrogen

Internal energy, enthalpy, specific heat at constant volume,  $C_v$ , specific heat at constant pressure,  $C_p$ , and entropy can be calculated using Eqs. (58)–(62). The thermal EOS (273) together with equation for internal energy (58) or enthalpy (59) determines the parametric relationships  $p$ - $\rho$ - $E$  or  $p$ - $\rho$ - $H$ , respectively, with temperature serving as a parameter.

## CHAPTER 8: MIXING RULES

The problem of obtaining the EOS for a mixture of several gaseous species based on available equations of state for individual species has an exact solution only in one limiting case—for a rarefied gas in which interaction between molecules is insignificant and therefore for the gas which can be treated as ideal. In this case, the Dalton law on additivity of partial pressures is valid for mixture and the total pressure in the mixture is given by the Clapeyron equation:

$$p = nRT,$$

where  $n$  is the number of moles per unit volume which is independent of relative species concentrations.

In real gases, pressure at given  $T$  and  $\rho$  depends on interaction between molecules, including interactions between molecules of different species. Streakly speaking, this interaction cannot be reduced to consideration of interaction between molecules of each species taken separately. Therefore the problem formulated above can be solved only approximately. Moreover, the approximation error will be different for different mixtures and hence cannot be estimated precisely.

In practical applications dealing with thermodynamics of natural gases and oils, various concepts of constructing the EOS for mixtures are used which are

**Table 33.** Values of coefficients  $b_i$  for species under study

Species	H <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>
$b_i, \text{dm}^3/\text{mol}$	0.0244	0.0396	0.0353	0.0306	0.0379	0.0394

based on approximate scaling laws, pseudocritical parameters, etc. [6, 18]. Due to complicated formulations and extended correlations, such concepts are not feasible for CFD applications.

If the EOS for gaseous mixture is taken in a virial form, the problem is reduced to obtaining the dependencies of virial coefficients on individual species concentrations. In this case, a general relationship for the second virial coefficient is given by [54]:

$$B_{mix} = \sum_{i,k}^N B_{ik} x_i x_k, \quad (313)$$

where  $N$  is the number of species in the mixture,  $x_i$  are the relative (normalized to unity) species concentrations, and each diagonal element  $B_{ii}$  is the second virial coefficient of individual species. The problem which can be solved only approximately is to determine nondiagonal elements  $B_{ik}$  in terms of the corresponding diagonal virial coefficients  $B_{ii}$  and  $B_{kk}$ . For two-parameter equations of state of Van-der-Waals type with parameters  $a$  and  $b$  (in common notations), the following mixing rules are usually applied [6]:

$$b_{mix} = \sum_i^N b_i x_i, \quad a_{mix} = \sum_{i,k}^N a_{ik} x_i x_k, \quad (314)$$

$$a_{ik} = \sqrt{a_i a_k}. \quad (315)$$

The form of the virial EOS used herein in Chapters 1 to 7 is also of Van-der-Waals type with truncated virial series where

$$B = b - a^*, \quad a^* \equiv a/RT. \quad (316)$$

Therefore, for gaseous mixture one can write

$$B_{mix} = b_{mix} - a_{mix}^*. \quad (317)$$

Applying first formula of Eqs. (314), rewritten in the form

$$b_{mix} = \sum_{i,k}^N b_i \delta_{ik} x_i x_k, \quad (318)$$

where  $\delta_{ik}$  is Kronecker delta, one obtains from Eq. (317) and second formula of Eqs. (314):

$$B_{mix} = \sum_{i,k}^N (b_i \delta_{ik} - a_{ik}^*) x_i x_k. \quad (319)$$

Comparison of Eqs. (319) and (313) gives:

$$B_{ik} = b_i \delta_{ik} - a_{ik}^*. \quad (320)$$

Taking into account Eqs. (315) and (316), one finally arrives at formula

$$B_{ik, i \neq k} = -\sqrt{(b_i - B_i)(b_k - B_k)}. \quad (321)$$

Our calculations of coefficients  $b$  and  $B$  as functions of temperature for all species of interest indicate that differences  $b_i - B_i$  are positive within the entire temperature range (up to 3000 K) for steam, carbon monoxide, carbon dioxide, hydrogen, and nitrogen. For oxygen, this difference changes sign at temperature of about 2200 K. As a result, the coefficient of Eq. (321) tends to zero and remains relatively small with further temperature increase. For alkanes, the corresponding change of sign occurs at ~890 K for methane, ~1200 K for ethane, ~1600 K for butane, and ~1900–2000 K for other alkanes except for propane. For propane, the sign of coefficient under consideration remains positive within the entire temperature range. Keeping in mind that the EOS for alkanes is of primary interest at temperatures up to approximately 1000 K, it is worth to use the absolute value of expression under the square root of Eq. (321) to avoid formal mathematical problems in computational routines, i.e.,

$$B_{ik, i \neq k} = -\sqrt{(b_i - B_i)(b_k - B_k)}. \quad (322)$$

Note that nondiagonal elements of Eq. (322) are always negative. This result is difficult to interpret in terms of realistic interactions between molecules of different species as it is a consequence of groundless application of mixing rule (315) to coefficients  $a_i$  for the case when they are temperature dependent. At low temperatures, when coefficients  $B_i$  are negative and their absolute values are large as compared to  $b_i$ , Eq. (322) is reduced to

$$B_{ik, i \neq k} = -\sqrt{B_i B_k}. \quad (323)$$

Low-temperature approximation of Eq. (323) looks physically justified.

At high temperatures, second virial coefficients of individual species are positive, depend weakly on temperature, and are close to coefficients  $b_i$  according to their physical meaning. Therefore at high temperatures a linear approximation seems to be appropriate, similar to the first formula of Eq. (314):

$$B_{mix} = \sum_i^N B_i x_i. \quad (324)$$

We suggest to use Eq. (324) as a simple and uncontradictory mixing rule within the entire temperature range from 280 to 3000 K. Thus, we recommend using the EOS in the form

$$p = \rho RT [1 + B\rho + b^2 \rho^2 + b^3 \rho^3], \quad (325)$$

where  $\rho$  is the molar density of mixture (number of moles of mixture in unit volume), with linear combi-

nations of coefficients  $B_i$  and  $b_i$  in terms of concentrations:

$$b_{mix} = \sum_i^N b_i x_i, \quad B_{mix} = \sum_i^N B_i x_i. \quad (326)$$

Parameters  $B_i$  and  $b_i$  as functions of thermodynamic state were determined in the corresponding Chapters of this paper. In those cases when coefficients  $b_i$  depend on temperature and density (alkanes) we recommend to use mixture density rather than partial density for their calculation.

Reliability of any averaging procedure increases with decreasing the variance of numerical data. The variance of coefficient  $b_i$  is relatively small. For all species of interest these coefficients are not only of the same order of magnitude, but their numerical values are very close to each other (Table 33).

One may assume that at such a small variance the use of the mean arithmetic value of  $b_i x_i$  (Eq. (326)) as an effective value of  $b_{mix}$  in the EOS for mixture will result in insignificant errors. However, in case of alkanes, coefficients  $b_i$  entering our EOS, depend on density. As a result, some uncertainty exists in selecting density in the expression for  $b_i$  at given values of temperature  $T$  and density  $\rho$ : one can use either mixture density or partial density of the  $i$ th species. Obviously, any selection leads to errors which are hardly controlled.

In view of it, when dealing with mixtures, it seems reasonable to simplify the EOS for alkanes by neglecting the dependency of coefficient  $b_i$  on density and therefore allowing for certain deterioration in accuracy. As for the second virial coefficients  $B_i$ , their values are close to  $b_i$  at high temperatures (see the discussion above). Therefore at high temperatures, the variance of coefficients  $B_i$  is also small and, similar to the case with coefficients  $b_i$ , there are strong grounds to believe that the use of the arithmetic mean  $B_i x_i$  in Eq. (326) is justified.

At low temperatures, the calculation of  $B_{mix}$  using Eq. (326) may result in errors of tens of percent. In terms of pressure, cold isothermal compression at low temperatures can result in errors up to 10%. However the parametric domain with high pressure and low temperature is virtually out of interest for practical applications dealing with piston engines. In these applications, low temperatures are associated with low pressures and thermodynamic properties of gaseous mixtures are close to those of ideal-gas mixture.

## CONCLUDING REMARKS

Analytical approximations developed within this paper are rather simple and therefore can be used directly in CFD codes.

Application of the EOS in the form of Eq. (19) to all  $n$ -alkanes, except for  $n$ -butane chosen as a "standard" gas, should be treated as extrapolation. This

extrapolation is based on the assumption that deviation from the law of relative states can be taken into account only by the second virial coefficient, at least at relatively low densities ( $\rho/\rho_c \approx 0.3-0.5$ ). This extrapolation is rather gallant. Nevertheless, it does not result in considerable errors for  $n$ -alkanes from methane to  $n$ -heptane (see Table 3). For higher  $n$ -alkanes, there are no experimental  $p-v-T$  data available for direct comparison with the EOS proposed herein.

The use of the second virial coefficient with regard for the Pitzer factor (see Chapter 1) and a nondeteriorating accuracy of predicted pressure in critical points of high  $n$ -alkanes as compared to low  $n$ -alkanes, may serve a ground to hope that the accuracy of Eqs. (19) for high  $n$ -alkanes is quite reasonable.

Errors inherent in the EOS for individual species (e.g., error associated with predicting pressure as a function of temperature and density) lead to errors in calculated excess thermodynamic functions and specific heats ( $E_{exc}$ ,  $H_{exc}$ ,  $S_{exc}$ ,  $C_{v,exc}$ ,  $C_{p,exc}$ , etc.). The latter errors are determined by the errors in virial coefficients. At relatively low gas densities, which are of primary interest for piston engine applications, these are mostly due to errors in the second virial coefficients.

Analytical expressions for the second virial coefficients developed in this paper or taken from the literature (for alkanes and oxygen) as well as tabulated data in handbooks have an average error of the order of several percent. Correspondingly, thermodynamic functions  $E_{exc}$  and  $H_{exc}$ , which depend on the first derivatives of virial coefficients, can exhibit errors that are several times larger (by a factor of 2 to 3, in average). However in the thermodynamic domain of interest, the contribution of these excess functions to the total energy  $E$  and enthalpy  $H$  is small as compared with the contribution of ideal-gas components  $E_0$  and  $H_0$ . By the order of magnitude, their contribution is of order 0.1 at low temperatures and high pressures ( $\sim 20$  MPa) and 0.01 at high temperatures and high pressures, decreasing along isotherms with pressure (density) drop. Therefore relatively high errors in the second virial coefficient mentioned above lead to considerably smaller (by a factor of 10 to 100) errors in excess functions  $E_{exc}$  and  $H_{exc}$ .

Excess specific heats  $C_{v,exc}$  and  $C_{p,exc}$ , which depend on the first and second derivatives of virial coefficients, are determined with the same or somewhat larger errors as those relevant to  $E_{exc}$  and  $H_{exc}$ , however the contribution of  $C_{v,exc}$  and  $C_{p,exc}$  to total specific heats  $C_v$  and  $C_p$  does not exceed several percent even at pressure of 20 MPa. For example, at temperature of 300 K and pressure of 20 MPa, the specific heat of nitrogen  $C_v$  is 21.85 J/(mol K) [33]. This value is only by 1 J/(mol K) higher than the ideal-gas specific heat  $C_{v0}$  at similar conditions, i.e., by 5%. At a temperature of 1200 K and pressure of 20 MPa, the difference between  $C_v$  and  $C_{v0}$  is equal to  $C_{v,exc} = (25.55-25.41) = 0.14$  J/(mol K), i.e., only 0.5%. Therefore the relative error of total specific heats in the

thermodynamic domain of interest attains average values of tenth fractions of percent with the maximum values of about 1 to 3%.

In conclusion, it is worth mentioning that irrespectively of accuracy provided by  $p$ – $v$ – $T$  EOS, one of the most important issues for CFD practice is the consistency of thermodynamic parameters used. In the absence of such consistency, the energy conservation law will fail. If excess thermodynamic parameters ( $E_{exc}$ ,  $H_{exc}$ ,  $S_{exc}$ ,  $C_{v, exc}$ ,  $C_{p, exc}$ , etc.) are expressed analytically based on the thermal equation of state used in calculations, the requirement of thermodynamic consistency is met automatically. Our analytical EOS in the form of virial series together with the analytical dependencies of virial coefficients on temperature guarantee such automatic consistency.

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